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Evaluation of Methods for the Determination of Total Organic Halide in Water and Waste

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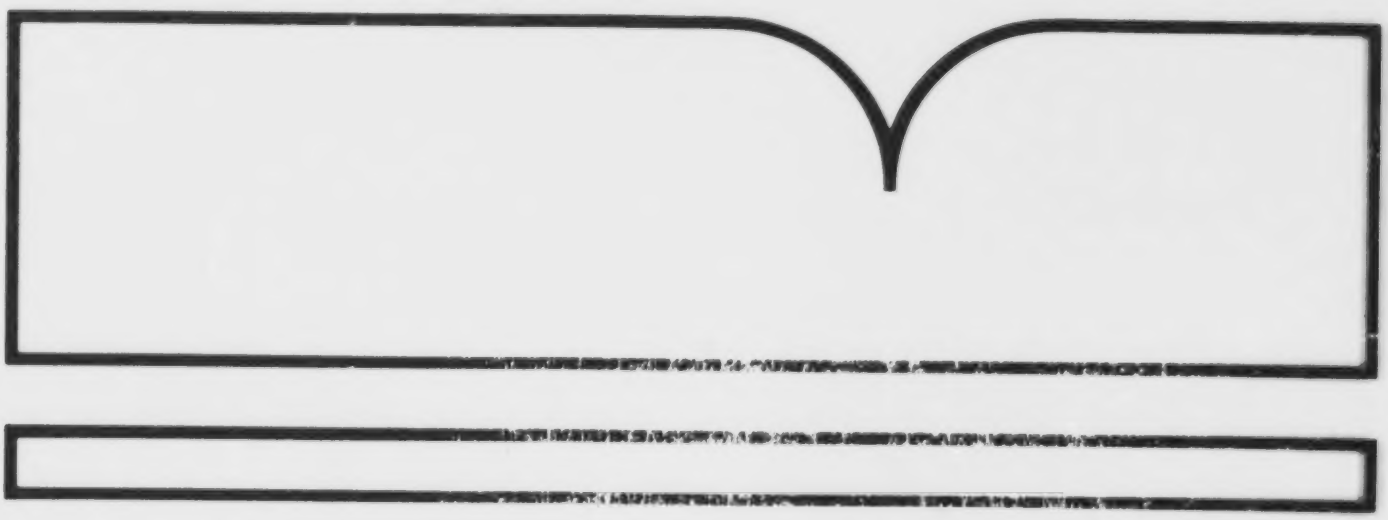

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EVALUATION OF METHODS FOR THE DETERMINATION OF TOTAL ORGANIC HALIDE IN WATER AND WASTE

by

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Various methods for the determination of total organic halides (TOX) in groundwater and in waste oil samples have been evaluated. Of three inorganic halide species generation approaches and three inorganic halide determinative techniques evaluated for groundwater analyses, one combined approach using Schoeniger flask oxidation with colorimetric chloride determination was chosen for laboratory validation and method detection limit studies. Groundwater samples were also analyzed for TOX using neutron activation analysis.

A method for analysis of oil samples which uses the sodium biphenyl reagent and a colorimetric chloride method was found to be unsatisfactory for the analysis of various oils spiked with PCBs due to interferences in the colorimetric determinative step which resulted in recoveries greater than 100%.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report presents the results of the evaluations of several methods for the determination of total organic halide in environmental samples.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

Various methods for the determination of total organic halides (TOX) in groundwater and in waste oil samples have been evaluated. Of three inorganic halide species generation approaches and three inorganic halide determinative techniques evaluated for groundwater analyses, one combined approach using Schoeniger flask oxidation with colorimetric chloride determination was chosen for laboratory validation and method detection limit (MDL) studies. Groundwater samples were also analyzed for TOX using neutron activation analysis.

The Schoeniger flask/colorimetric chloride and neutron activation analysis methods were found to give TOX results for spiked groundwaters which were comparable to those obtained using Interim Method 450.1. However, the Schoeniger flask/colorimetric halide method was useful only for halide levels above 0.2 mg/L due to high halide background levels encountered in the reagents.

A method for analysis of oil samples which uses the sodium biphenyl reagent and a colorimetric chloride method was found to be unsatisfactory for the analysis of various oils spiked with PCB's due to interferences in the colorimetric determinative step which resulted in recoveries greater than 100 percent.

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SECTION 1

INTRODUCTION

This program is a continuation of EPA Contract 68-03-2984, "Surrogate Methods for Priority Pollutants in Wastewater" (1). The objective of the work conducted under this research program was to evaluate additional direct and indirect methods for TOX analysis.

Indirect methods which were evaluated included Parr bomb oxidation, Schoeniger flask oxidation, and sodium biphenyl dehydrohalogenation as species generation approaches for conversion of organic halide to inorganic halide. The determinative techniques evaluated for the inorganic halide produced included ion chromatography, chloride ion selective electrode, and a colorimetric halide procedure. In all cases, the sample preparation procedure used was the charcoal adsorption technique from Interim Method 450.1 (2). The primary thrust of this portion of the program was to select the best species generation approach and best determinative technique, and to combine these approaches into a TOX method for use as a less costly alternative to the microcoulometric determinative technique of Interim Method 450.1.

Neutron activation analysis using the sample preparation procedure from Interim Method 450.1 was the only direct approach evaluated. This method was chosen for its ability to distinguish between the various halogen species at parts-per-million levels.

In addition to the above methods for the analyses of TOX in aqueous samples, the sodium biphenyl reagent approach was evaluated for the analysis of TOX in transformer oil samples. The determinative technique for these evaluations was the colorimetric chloride method used for the aqueous sample analyses.

SECTION 2

CONCLUSIONS

Based on the results presented in subsequent sections, several important conclusions may be drawn concerning the methods for the determination of TOX which were evaluated under this program:

- The Schoeniger flask oxidation method is the most appropriate approach of those evaluated for species generation. However, high background and reagent halide levels limit the usefulness of this method to TOX levels near or above 0.2 mg/L in surface waters.

- The ion chromatographic method and the colorimetric chloride method give comparable results for spiked samples analyzed using the two approaches. The colorimetric method was chosen for the determinative technique since it requires less sophisticated instrumentation. Halide speciation cannot be achieved using ion chromatography due to the nitrate interferences encountered in extracts produced using the charcoal adsorption procedure from Interim Method 450.1, which effectively prevents the determination of bromide in these extracts.

- The ion selective electrode is not suitable for halide analyses of samples prepared using the Schoeniger flask oxidation approach.

- The neutron activation analysis procedure gives results comparable to those obtained using Interim Method 450.1 for spiked groundwater samples. In addition, the method is able to quantify both chloride and bromide in the same analysis.

- The sodium biphenyl reagent species generation procedure and colorimetric halide determinative method is unsuitable for waste oil analyses in its present form. Interferences from the oil samples result in high recoveries for various oil samples spiked with PCB's.

SECTION 3

RECOMMENDATIONS

Based on the results of spiked reagent water and groundwater samples analyzed using the Schoeniger flask oxidation and colorimetric halide TOX procedure evaluated under this program, this method is recommended as an alternative to Interim Method 450.1 for use as a TOX screening method for aqueous matrices, with the caveat that this procedure is applicable only to levels of TOX at or above 0.2 mg/L in aqueous matrices. This method provides a significantly less costly alternative for the analysis of samples which contain low parts-per-million levels of organic halogen and gives results which are comparable to Interim Method 450.1.

The results of the evaluation of EPA Method 9022, Total Organic Halides by Neutron Activation Analysis, indicate that this direct method also is an appropriate technique for TOX analysis and offers the additional advantage of providing individual chlorine and bromine values for the sample at levels equal to TOX detection limits achievable with the microcoulometric determinative technique of Interim Method 450.1.

The experiments conducted using the sodium biphenyl reagent and colorimetric halide determinative technique for the analysis of total organic chloride from oil matrices indicate that this procedure is not suitable as a screening procedure in its present form. Further evaluation of the sodium biphenyl reagent with some alternative determinative technique, such as microcoulometric titration, or with some additional cleanup step for the extract prior to the colorimetric determinative step is necessary to establish the usefulness of this technique at those halide levels in the range of from 20 to 350 µg/g, as were evaluated in this study.

SECTION 4

EXPERIMENTAL PROCEDURES

TASK 1: EVALUATION OF THE OXIDATION APPROACH

Three oxidation approaches were evaluated under Task 1 for the conversion of organic chlorine to chloride ion: Schoeniger flask combustion, Parr bomb combustion, and sodium biphenyl dehydrohalogenation. The reference determinative technique for the comparisons was ion chromatography, described under Task 2, except for the sodium biphenyl approach for which ion chromatography was not suitable due to interferences caused by high nitrate concentrations. In this case the ASTM D-512, "Standard Test Method for Chloride Ion in Water and Wastewater" colorimetric method was used (3).

Evaluation of the Schoeniger Flask Oxidation Procedure

The reference procedure used in the evaluation of the Schoeniger flask oxidation approach was derived from ASTM E442, "Standard Test Method for Chlorine, Bromine, or Iodine in Organic Compounds by Oxygen Flask Combustion" (4).

Forty (40) mg of granulated activated charcoal was wrapped in two black sample wrapping papers (Arthur H. Thomas, catalog number 6514-F70) and suspended in the oxidation flask. The absorbing solution used in all experiments with the combustion flask was 10.0 mL of 0.10N potassium hydroxide (KOH, J. T. Baker Chemical Company, ACS reagent grade). The flask was flushed with oxygen for five minutes, sealed, and ignited using an infrared igniter in a fume hood. The flask was allowed to stand for 60 minutes with occasional shaking before transferring the absorbing solution to an acid rinsed (10 percent HNO_3) vial equipped with a Teflon-lined screw cap for storage prior to ion chromatographic (IC) analysis. All combustion apparatus was rinsed with 10 percent aqueous HNO_3, distilled water, and high

purity charcoal filtered deionized water prior to oven drying (110°C) and reuse. Replicate blank determinations of the black wrapping paper and all reagents were prepared in the same manner.

In the initial spiking experiments chloride was the only halide studied. The spike solution was prepared by weighing 0.3723 g of 2,4,6-trichlorophenol into a 10.0 mL volumetric flask and diluting to volume with reagent grade methanol (chloride concentration = 20 µg/µL). Replicate samples of granulated activated charcoal were spiked with 5.0 µL of the above spike solution (100 µg as Cl) and processed as described above. Hydrogen peroxide (three drops) was added to the samples to oxidize any bromide or iodide to bromate or iodate prior to storage.

The spiking solution used in all subsequent experiments was a 20 mg/mL (20 µg/µL) halide stock solution containing 90 percent of the halide as chloride and 10 percent as bromide. The halide proportions were 45 percent as chloride derived from tetrachloroethylene, 45 percent as chloride from 2,4,6-trichlorophenol, and 10 percent as bromide from bromoform as requested by the project officer. The concentration of this spiking solution was verified by analysis of blank granulated activated charcoal (GAC) spiked with 1.0 µL of the 20 µg/µL halide stock from a 20.0-µL syringe using the Dohrmann Model DX-20 Microcoulometric Detector. Additional modifications to the above sample preparation procedure included the use of a single sheet of the black wrapping paper for sample combustion, and the elimination of the hydrogen peroxide oxidation step.

Eight samples were prepared for the evaluation of the Schoeniger flask oxidation approach evaluations: two blank charcoal samples, three low level spiked charcoal samples containing 100 µg halide (5.0 µL of the 20 µg/µL spiking solution), and three high-level spiked charcoal samples containing 500 µg halide (25.0 µL of the 20 µg/µL spiking solution). All samples contained one piece of black wrapping paper and 40 mg of charcoal and were absorbed into 10.0 mL of 0.1N KOH solution in the oxidation flask. The samples were analyzed using the ion chromatographic procedure described below under Task 2 studies.

Three additional experiments were performed which related specifically to the Schoeniger flask technique. The first experiment was an attempt to reduce the chloride blank level in the black wrapping paper by washing in a Buchner funnel with 100 mL of 8.2 g/L KNO_3 solution. Sample papers were rinsed with distilled water and partially dried at 110°C for 15 minutes prior to halide determination using the Dohrmann Microcoulometric detector.

The second experiment was designed to evaluate the effectiveness of hydrazine in reducing bromate ion to bromide. The ASTM procedure which was used for all Schoeniger flask oxidations gives two options for halide sample preparation. The first option is to use hydrogen peroxide to oxidize bromide or iodide to the bromate or iodate if the only interest is in the chloride content of the sample. The second option is to use hydrazine sulfate ($NH_2NH_2 - H_2SO_4$) for the reduction of any oxidized bromine or iodine species which may be produced in the combustion to the bromide or iodide ion. Preliminary work using the hydrazine sulfate reduction procedure had indicated that the high levels of sulfate in the reagent would cause problems in the IC analysis of the samples and require dilutions. Because of the level of bromide spiked in the sample, sensitivity considerations using the IC method would not allow a significant dilution of the sample. The reduction experiments were accomplished by adding 10.0 µL of neat hydrazine liquid (Eastman-Kodak) to 10 mL of 0.1N KOH containing 5 mg of potassium bromate (J. T. Baker Co.) and allowing to stand for 15 minutes prior to bromide analysis using IC.

During the analysis of the spiked samples prepared using the Schoeniger flask method, high nitrate levels were found to prevent the quantification of bromide ion when using the IC determinative technique. In order to determine the source of the nitrate interference, a third experiment was performed in which a series of samples was prepared in glassware that had been cleaned using a procedure that would eliminate any possible nitrate interference from the cleaning procedure used previously. Originally the glassware used for the Schoeniger flask samples was cleaned by soaking the glassware in dilute nitric acid until it was needed. The glassware was rinsed with distilled water followed by reagent water that had been passed through a charcoal column and was dried in an oven at 100°C. The new procedure called for a

0.1N KOH rinse, followed by a second rinse with distilled water and reagent grade water prior to drying. The samples prepared in the glassware included a reagent blank, three replicates of Whatman 541 filter paper, three replicates of Whatman 541 filter paper with 40 mg of charcoal, and one sample of black wrapping paper with 40 mg of charcoal. The Whatman 541 filter paper samples were ignited using a small strip of black wrapping paper.

Evaluation of the Parr Bomb Oxidation Procedure

The standard procedure used in the preparation of all samples with the Parr Bomb was derived from ASTM Method D3761-79, "Standard Test Method for Total Fluorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method," (5), with minor modifications. These modifications included the use of a combustion bomb equipped with a quartz liner, (Parr Institute Co.), the substitution of 0.1N KOH for the recommended 1N sodium hydroxide absorbing solution, and the use of an oxidation accelerator solution of 1 percent collodion (a nitrocellulose preparation) in amyl acetate. The 0.1N KOH absorber solution had been used successfully in the Schoeniger flask procedure and was more compatible with the IC determinative procedure than the higher concentration NaOH absorber solution recommended in the method. The 1 percent collodion accelerator was necessary due to problems in igniting the small 40 mg quantities of granulated activated charcoal. The use of the quartz-lined Parr Bomb was necessary due to the highly colored absorber solutions which resulted when using only the stainless steel portions of the bomb. The dark green absorbing solutions obtained after ignition were anticipated to interfere with the colorimetric method. Since the metals content was not accurately known, this was also a possible interference with the ion specific electrode determinations to be performed under Task 2.

The interior of the Parr Bomb, the quartz sample holder, the quartz collector, and quartz holder lid were all washed with concentrated HNO_3, rinsed with deionized water, and dried in a drying oven at 105°C prior to each use. Forty (40) milligrams of granulated activated charcoal was placed in the collector and the platinum firing wire situated in contact with the charcoal. If the sample was to be spiked, 5.0 µL of the 20 µg/µL halide

spiking solution (described above for the Schoeniger flask method and equivalent to a 100 µg halide level) was added to the charcoal. Six drops (approximately 50 µL) of a 1 percent collodion solution in amyl acetate was added at this time to assist in the ignition of the sample. A 5.0-mL aliquot of the 0.1N KOH absorber solution was added to the quartz sample holder; the bomb was assembled and charged with 30 atmospheres of oxygen. After ignition, the bomb was allowed to stand for 15 minutes to allow the vapors to be absorbed into the 0.1N KOH, as prescribed by the method. The bomb was then opened and the KOH solution quantitatively transferred to a clean, dry 10 mL volumetric flask and diluted to volume with 0.1N KOH absorbing solution. Eight samples were prepared, including three charcoal method blanks, three spiked charcoal samples fortified with 100 µg total halide, and two charcoal blanks which were fired without the use of the quartz sample collector insert. Samples were analyzed by IC using the conditions described below.

One additional experiment was performed. Forty (40) milligrams of granulated activated charcoal was spiked with 25.0 µL of the 20 µg/µL halide spiking solution (equivalent to 500 µg of total halide) and prepared according to the above procedure, with the exception that the absorption time was extended to one hour instead of the 15 minutes used for the previous samples.

Evaluation of the Sodium Biphenyl Reagent Procedure

The use of the sodium biphenyl reagent for TOX determination was evaluated for halide recovery using the ASTM colorimetric method for the quantification of total halide in the extract. The method was evaluated for both halide standards in methanol and for standards spiked onto granulated activated charcoal.

Organic halogen reagent, sodium biphenyl solution, was obtained from Southwestern Analytical Chemicals Incorporated of Austin, Texas. The spiking solution used in all experiments was the three component mixture described on page 5. One container of the reagent (approximately 15 mL) was placed in a clean glass separatory funnel. Three replicates each of method blanks and

samples spiked at 500 µg halide level were prepared by adding 25.0 µL of the spiking solution directly to the sodium biphenyl reagent in the separatory funnel. The solution was mixed by swirling and allowed to stand for two minutes to ensure complete reaction. After two minutes, 2 mL of 2-propanol was added to destroy the excess reagent. Then 2 mL of toluene was added and the samples were extracted with three consecutive 5-mL portions of 3N nitric acid. The extracts were collected in a 25.0 mL volumetric flasks and brought to volume with 3N nitric acid.

Spiked charcoal samples were prepared at the 100 µg halide level by the addition of 5.0 µL of the spike solution to 40 mg of the granulated activated charcoal on an aluminum foil sample holder. The spiked sample was allowed to air dry for 20 minutes prior to the addition to the separatory funnel containing the sodium biphenyl reagent. Three unspiked charcoal samples were also prepared, and the samples were extracted as described above. Samples were analyzed using the ASTM D-512 Colorimetric Method described below under Task 2.

After the initial experiments using spiked charcoal, a series of spiked distilled water samples were prepared using the charcoal adsorption procedure from Interim Method 450.1 and processed using the sodium biphenyl reagent method.

Reagent water samples spiked at the 500-µg level were prepared by adding 25 µL of the spiking solution described above to 120 mL of reagent water in a 4-oz glass bottle equipped with a Teflon-lined screw cap. The sample was stirred gently with a stir bar for three to five minutes, adjusted to pH 2 with nitric acid, and added to the adsorption module. One hundred mL of the sample was passed through two charcoal adsorption traps in series, each of which contained 40 mg of granulated activated charcoal and had been washed with 2 mL of 8200 mg/L KNO_3 prior to use. After eluting 100 mL of the sample, the adsorption traps were rinsed with 2.0 mL of 8200 mg/L KNO_3 and the charcoal from the primary adsorption tube transferred to a 60-mL separatory funnel containing 15 mL of sodium biphenyl reagent (Southwestern Analytical Chemicals, Inc.) and 2 mL of toluene.

The solution in the separatory funnel was mixed by swirling and allowed to stand for two minutes to ensure complete reaction. After two minutes, 2 mL of 2-propanol was added to destroy the excess reagent, and the sample was extracted with three consecutive 5-mL portions of 3N nitric acid.

The extracts were collected in 25.0 mL volumetric flasks and brought to volume with 3N nitric acid. Nine samples were prepared, including two unspiked charcoal samples, three spiked (500 µg) charcoal samples prepared using the adsorption module, one backup module from a spiked sample, and three charcoal samples spiked directly with the halide mixture described above. Immediately prior to colorimetric analysis, a 10-mL portion of the sample was shaken with 10 mL of reagent grade toluene in a Teflon-lined screw cap vial. A portion of the aqueous phase was then processed for colorimetric analysis.

TASK 2: EVALUATION OF THE DETERMINATIVE TECHNIQUE

Under Task 2, three determinative techniques for chloride ion were evaluated. These techniques included ion chromatography (IC) (6), chloride ion specific electrode (ISE), and the ASTM D-512 colorimetric chloride method.

The initial evaluations consisted of analysis of spiked reagent water replicates generated using the most appropriate species generation approach from Task 1.

Evaluation of Ion Chromatography as the Determinative Technique

Initial evaluations of the IC determinative technique included an evaluation of sensitivity and linearity of response over an appropriate range of chloride concentrations. The chromatographic conditions for these initial evaluations were as follows:

Ion Chromatograph -- Dionex Model 16
Columns -- Dionex S_2 and Dionex S_1
Flow Rate -- 3.0 mL/min (S_2 column) and 2.0 mL/min (S_1 column)
Buffer -- 0.003M $NaCO_3$/0.002M NaOH
Detector -- Specific conductivity

Injection volume -- 100 µL
Attenuation -- 300, 30, and 10 µ mho full scale

IC was evaluated using the S_2 column over two chloride concentration ranges: 0.1 to 0.35 µg/mL Cl^- and 2.0 to 10.0 µg/mL Cl^-. The low level calibration curve was used for the analysis of blank samples where no dilution was required, and the higher level calibration was used for samples which contained higher concentrations of analyte.

The linearity of response for chloride and bromide determinations over the range of 2 to 10 µg/mL was also evaluated on the S_1 column, as well as the separation of six common anions.

Evaluation of the Chloride Ion Specific Electrode Technique

The chloride ion specific electrode (ISE) was initially evaluated for linearity of response over the 1 to 100 µg/mL calibration range for both chloride and bromide ions. The equipment used in these evaluations and in the analysis of the sodium biphenyl reagent spikes and blank samples was as follows:

- pH meter - Corning Model 125
- Chloride electrode - Orion Model 94-17B
- Reference electrode - Corning reference electrode (Cat. no. 476002)
- Temperature - ambient, normally 27°C

An ionic strength adjusting solution of 5M sodium nitrate and 0.15M HNO_3 (Orion catalog no. 94-0009) was used prior to making all measurements. Samples and calibration standards were prepared by adding 2.0 mL of the solution to be measured to 2.0 mL of the ionic strength adjusting solution in the sample container used for the readings. The electrodes were immersed in the solution and the sample stirred continuously for 10 minutes, at which time the millivolt reading was taken from the meter.

After the initial evaluations for detection limit and response, two sets of spiked charcoal samples were analyzed which had been prepared using the Schoeniger flask oxidation procedure described under Task 1. The spike

levels for these samples were 100 and 500 µg, respectively, onto 40 mg of granulated activated charcoal, and were prepared and analyzed as described above.

After the analysis of the samples by ISE, the 4- and 10-µg/mL calibration standards and one each of the 100 and 500 µg halide spiked samples were reanalyzed by IC. These analyses were necessary in order to determine if the readings obtained initially had changed since the samples were first prepared and analyzed.

Evaluation of the ASTM D-512 Colorimetric Chloride Determinative Technique

The ASTM D-512 Colorimetric Method for Chloride Ion in Water and Wastewater was evaluated for reagent blank levels, chloride and bromide response, and for the effect of nitrite interference on the colorimetric procedure.

A Bausch and Lomb Spectronic 21 digital visible spectrophotometer equipped with 10 mm I.D. test tube-type cuvettes was used for all colorimetric determinations, using a wavelength of 463 nm as specified in the method. Due to the small volume of sample expected from Schoeniger flask and Parr bomb sample preparations (10 mL), the sample size was reduced to 5.0 mL instead of the 25 mL sample recommended in the colorimetric procedure. The volumes used of the two color-producing reagents, 50 g/L ferrous ammonium sulfate and 3 g/L mercuric thiocyanate, were also reduced five-fold. No other modifications to the method were made.

For all determinations, 5.0 mL of the sample to be measured for chloride was placed in a clean, dry 50-mL test tube and 1.0 mL of ferric ammonium sulfate solution was added. The sample was mixed on a vortex mixer, 0.50 mL of mercuric thiocyanate solution was added, and the solution was again mixed on a vortex mixer. The sample was allowed to stand for 10 minutes for color development, transferred to a sample cuvette, and the absorbance was measured on the spectrophotometer. Calibration curves were prepared from zero to 100 µg/mL chloride and nitrite, and 1.0 to 40 µg/mL bromide. In addition, duplicate samples were prepared containing 100 µg/mL nitrite and 10 µg/mL chloride to assess the effect of nitrite on chloride color development.

Spiked Charcoal Sample Analyses--

Blank and spiked granulated activated charcoal samples which were prepared using the Schoeniger flask oxidation procedure were analyzed using the ASTM Colorimetric procedure in order to compare the colorimetric results with those obtained using the IC and ISE.

The spiked samples included three replicates of granulated activated charcoal spiked at the 100 µg chloride level (as trichlorophenol), and three replicates each of sample spiked at the 100 and 500 µg total halide level using the three component spiking solution containing both chloride and bromide described above. Appropriate reagent blank samples were also evaluated for the two different sets of spiked samples, since the sample spiked with chloride only was prepared using two sheets of black wrapping paper while the samples spiked with both chloride and bromide were prepared using only one sheet of black wrapping paper.

All samples were analyzed using the ASTM D-512 Colorimetric Method as described above. The calibration curve used for the determinations was prepared using the same procedure and consisted of solutions containing 0, 1, 4, 10, 20, and 40 µg/mL chloride.

Analysis of Samples Prepared Using Interim Method 450.1 Adsorption Procedure--

The Schoeniger flask oxidation procedure and the ASTM D-512 colorimetric chloride method were combined and used for the analysis of water samples prepared using the adsorption procedure from Interim Method 450.1.

Three water samples were prepared using the adsorption module procedure described under Task 1 including a reagent water sample spiked at the 50 µg/100 mL level, a domestic well water sample obtained from a drinking water well located near Hilliard, Ohio, which was spiked at the 500 µg/100 mL level, and a monitoring well groundwater sample obtained from a well in northern Alabama, which was spiked at the 100 µg/100 mL level. All samples were spiked with the 20 µg/µL spiking solution described above and 100 mL of sample was used in the charcoal adsorption procedure. In addition, these same samples were prepared for analysis using the Dohrmann microcoulometric halide method from Interim Method 450.1.

For the Schoeniger flask/colorimetric analysis samples, the adsorbed charcoal was removed from the primary cartridge and wrapped in a 1.5-inch square piece of Whatman filter paper (grade 541). The sample was then placed in a closed container overnight in order to allow the sample to dry partially before igniting in the Schoeniger flask as described above under Task 1.

A 1 mL to 5 mL dilution of the spiked domestic well water sample was required before color reagent addition. All samples were analyzed using the ASTM D-512 colorimetric method described above using a calibration curve of solutions containing 0, 5, 10, 15, 20, and 25 µg/mL chloride.

TASK 3: METHOD VALIDATION

Method Detection Limit for the Schoeniger Flask/Colorimetric Halide TOX Procedure

A MDL study was performed using the Schoeniger flask/colorimetric halide TOX procedure evaluated in this program using the standard EPA protocol (7).

Seven replicates of reagent water were spiked at the 0.51 mg/L halide level and 100 mL of sample was processed using the TOX procedure which is presented in Appendix A. Five replicates of 100 mL of unspiked reagent water were also prepared and analyzed for appropriate reagent background corrections.

Method Validation for the Schoeniger Flask/ Colorimetric Halide TOX Method and EPA Method 9022, TOX by Neutron Activation Analysis

Three identical sets of samples were prepared for validation of the methods evaluated in this program. One set was analyzed using the Schoeniger flask/colorimetric TOX Method, the second set was analyzed using EPA Method 9022, TOX by Neutron Activation Analysis which is described in Appendix B, and the third set was analyzed using Interim Method 450.1.

Sample Preparation

All samples in each set for the three methods were prepared in triplicate using the charcoal adsorption procedure from Interim Method 450.1 which is presented in Appendix C.

The samples (and sample volumes used in the adsorption procedure) included unspiked reagent water (100 mL sample), reagent water spiked at 0.51 mg/L (100 mL sample), unspiked groundwater (100 mL sample) from a monitoring well in Pennsylvania (groundwater #1), groundwater #1 spiked at the 0.51 (100 mL sample) and 1.02 mg/L (25 mL sample) halide levels, unspiked groundwater (25 mL sample) from a monitoring well in Alabama (groundwater #2), and groundwater #2 spiked at the 5.1 and 10.2 mg/L halide levels (10 mL samples each).

The spiking solution used in these preparations was the three component mixture described above under Task 1.

Sample Analysis

Samples for the Schoeniger flask/colorimetric TOX method and for Interim Method 450.1 analyses were processed in-house, while the samples for validation of the neutron activation analysis procedure were shipped by Federal Express to the Battelle Pacific Northwest Laboratories for analysis.

For analysis using the neutron activation analysis procedure, the charcoal sample in a two-fifths-dram polyvial was placed in the bottom of a two-dram polyvial and a weighed amount of approximately 10 mg of a copper flux monitor in a two-fifths-dram polyvial was placed above the sample in the vial. The sample and flux monitor were then irradiated for 15 minutes at a flux of 4×10^{12} neutrons/cm^2/sec. The irradiated two-fifths-dram polyvial containing the sample and the polyvial containing the copper flux monitor were each placed in clean nonirradiated two-dram polyvials. The sample was placed vertically in a holder 5 cm from the detector face of an upward-looking Intrinsic Germanium (IG) detector. After allowing for a 15-minute decay, the sample was counted for 1000 seconds with a dead time of less than 10 percent. The copper flux monitor was set aside for counting after all charcoal samples had been irradiated and counted.

The collected spectra (4096 channels, 1.0 KeV/channel gain) were then stored by a Tektronix recorder onto magnetic tape. The magnetic tape was subsequently read into a PDP 11/44 computer for data reduction by the program CANGAS (6). The copper flux monitors were also counted and the data reduced

so that a ratio to an arbitrarily chosen flux monitor was calculated. This ratio was then incorporated into the data reduction for each sample in order to account for any variation in neutron flux during irradiation of the samples.

TASK 4: EVALUATION OF INSTRUMENTAL METHODS

In the initial evaluation of the neutron activation analysis method for halides, a series of spiked charcoal samples was prepared to evaluate the detection limits for bromide and chloride on granulated activated charcoal. Samples were analyzed at the Battelle Pacific Northwest Facility using EPA Method 9022, Total Organic Halides (TOX) by Neutron Activation Analysis (Appendix B).

Sample Preparation and Analysis

The spiking solution used in these preparations was the three component mixture described above under Task 1. For the very low level spikes, a 1 to 10 dilution in methanol of the above stock solution was used.

Forty (40) milligrams of granulated activated charcoal was placed in the two-fifths-dram polyvials which had been cleaned by soaking in 6M HNO_3 overnight, followed by a distilled water rinse and air drying. The appropriate volume of spiking solution was then placed onto the charcoal and the vial sealed and placed in a cleaned two-dram polyvial in order to reduce the possibility of contamination. The five spike levels prepared ranged from 4.5 to 72 µg as chloride and from 0.5 to 8 µg bromide. Blank samples both with and without charcoal were prepared and all samples were prepared in triplicate.

Samples were stored until shipping in a 1-gallon can containing about 1 inch of activated charcoal in a solvent-free refrigerator, and were shipped via UPS to Dr. J. C. Laul at Battelle Pacific Northwest Laboratories. The charcoal sample in a two-fifths-dram polyvial was analyzed as described above under Task 3.

TASK 5: EVALUATION OF WASTE OIL METHODOLOGY

Ten PCB-spiked oil samples obtained from the U.S. EPA Quality Assurance Branch of the Environmental Monitoring and Support Laboratory at Cincinnati, Ohio were analyzed for organic chloride content using the sodium biphenyl reagent species generation method and the ASTM D-512 colorimetric chloride determinative technique. In addition to the oil samples, an analytical curve study was undertaken using a used transformer oil which had been spiked with Arochlor 1254.

Sample Preparation

The oil sample was weighed into a clean 25- or 50-mL volumetric flask and diluted to volume with distilled-in-glass toluene. A 5.0-mL aliquot of the sample in toluene was used for the analysis and each sample was prepared in triplicate. Samples were prepared by pipetting 5.0 mL of the toluene solution into a clean separatory funnel containing one 15-mL vial of sodium biphenyl reagent (obtained from Southwestern Analytical Chemicals, Inc., of Austin, Texas), and the sample was processed as described above under Task 1.

Eighteen oil samples were prepared, along with reagent blanks containing no oil, in triplicate. Immediately prior to colorimetric analysis, a 10-mL portion of the sample was shaken with toluene to remove coextracted biphenyl in a Teflon-lined screw cap vial. A 5.0-mL aliquot of the aqueous phase was then processed for colorimetric analysis as described above under Task 2.

Analytical Curve Study Sample Preparation

In addition to the above samples, an analytical curve study was undertaken to evaluate recoveries versus concentration with PCB-spiked transformer oil samples.

The transformer oil used was a General Electric oil which had been analyzed using gas chromatography with electron capture detection (ECD) and found to contain less than 5 ppm PCB's. The spiking solution used was a 12.5 mg/ml solution of Arochlor 1254 (Chem Service, Inc., F-111) in toluene. The spike solution was verified using the Dohrmann microcoulometric detector by placing a 5.0-µL aliquot onto 40 mg of granulated activated charcoal and

combusting the charcoal as described in Interim Method 450.1. Triplicate analyses were performed for the spiking solution and blank charcoal.

Samples were prepared by weighing 12.5-g aliquot of the transformer oil into each of six 25-mL volumetric flasks. Five of the flasks were then spiked with 100, 250, 500, 1000, and 2000 µL aliquots of the Arochlor 1254 spiking solution and brought to volume with distilled-in-glass toluene. A method blank consisting of distilled-in-glass toluene was also prepared. A 5-mL aliquot of each of the samples was then processed as described above for the PCB-spiked oil samples.

SECTION 5

RESULTS AND DISCUSSION

TASK 1: EVALUATION OF THE OXIDATION APPROACH

Evaluation of the Schoeniger Flask Oxidation Procedure

The results of the initial evaluations of the Schoeniger flask oxidation/IC approach with granulated activated charcoal are presented in Table 1. The results for reagent blanks using the Schoeniger flask combustion technique shown in Table 1 are quite low and represent the average amount of chloride contamination expected during the processing of a sample using this technique, exclusive of charcoal and wrapping paper. The black wrapping paper used for the sample combustion is the single largest contributor to the background, and averages 27 µg of chloride per sheet. In the experiments conducted to generate the data in this table, two pieces of wrapping paper were necessary to achieve complete combustion of the sample. Subsequent work showed that a single piece of paper can be used with careful wrapping technique; this lowered the blank chloride level to about 30 µg. The blank levels were confirmed using the Dohrmann microcoulometric detector, as shown in Table 2. These data show the charcoal blank level to be about 1 µg per 40 mg of charcoal and 22 µg per sheet black wrapping paper. This amount is equivalent to a blank level of 45 µg for 40 mg of charcoal and two pieces of black wrapping paper. The Dohrmann microcoulometric detector results are lower by 20 µg than those for the Schoeniger flask/IC technique, but also are subjected to fewer manipulations in the laboratory such as the transfers, dilutions, and filtrations required for IC analyses. After blank subtraction, the average recovery of spiked chloride using the Schoeniger flask procedure was found to be 78 percent with a standard deviation of 7.6 and a relative standard deviation of 9.8 percent. Chloride only (as trichlorophenol) was spiked in these samples in order to have a sample set

TABLE 1. RESULTS OF CHLORIDE ANALYSIS USING THE SCHOENIGER FLASK OXIDATION TECHNIQUE WITH ION CHROMATOGRAPHIC ANALYSIS

Sample Identification	Spike Level, µg Cl	µg Total Chloride in Sample				Standard Deviation	RSD, %	Average Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average			
Reagent Blank	0	2.2	1.7	2.7	2.2	0.50	23	NA(a)
Black Paper Blank(b)	0	52	57	55	55	2.5	4.6	NA
Charcoal & Black Paper Blank(b)	0	66	54	74	65	10	16	NA
Spiked Charcoal & 2 Sheets of Black Paper(c)	100	145	150	135	143	7.6	5.3	78(d)

(a) NA = Not applicable
(b) Two sheets of Black Wrapping Paper used in preparation of blanks and spikes.
(c) 100 µg of chloride spiked as trichlorophenol.
(d) A 9.8% relative standard deviation was obtained for the spiked sample.

TABLE 2. RESULTS OF HALIDE ANALYSIS OF BLACK WRAPPING PAPER AND CHARCOAL USING DOHRMANN MICROCOULOMETRIC DETECTOR

Sample Identification	Spike Level, µg Cl	µg Chloride in Sample				Average	SD	RSD, %	Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Replicate 4				
Boat Blank[a]	0	-0.13	0.00	0.04	0.00	--[b]	--	--	NA[c]
40 mg Charcoal Blank	0	1.2	0.86	0.95	0.96	0.99	0.15	15	NA
Black Wrapping Paper	0	29	23	19	19	22	4.7	21	NA
Spiked Charcoal	10	12	9.4	9.7	(d)	10	1.4	14	90[e]

(a) Analysis of sample boat without sample.
(b) Dash indicates not determined.
(c) NA = not applicable.
(d) Three replicates only.
(e) Average value after blank correction.

for comparison of IC with the ISE method (Task 2). The chloride level in the blanks limits the detection limit for this procedure value on the order of 0.5 to 1 mg/L. This estimate is based on the assumption that a 100-mL sample of water is concentrated onto 40 mg of charcoal and combusted using a single piece of black wrapping paper having a blank level of 20 to 30 µg of chloride. The precision of the Schoeniger flask/IC approach appears to be acceptable, but is limited by the wrapping paper blank, which has ranged from 19 to 29 µg per sheet as determined using the microcoulometric detector. The Dohrmann micro-coulometric detector was used throughout the program for evaluation of spike solutions and analysis of replicates of samples being analyzed using the evaluated methods.

The results of Schoeniger flask oxidation/IC experiments with charcoal spiked with the three component spiking solutions are presented in Table 3 and show good chloride recovery. These results indicate that the precision of the method is quite good at the levels spiked, even though the 100 µg spike level is only about twice the average background level of the method blanks. The method blanks, containing blank charcoal, one sheet of black wrapping paper, and all reagents averaged 19 µg lower than those shown in Table 1, where two sheets of sample wrapping paper were used. However, this blank level is still high and limits the Schoeniger flask oxidation approach to levels of halide on the order of 0.5 mg/L in the original water sample.

The bromide recoveries could not be determined using IC due to high nitrate levels encountered in the samples. In order to be able to determine bromide recovery, the level of bromide must be no less than 10 or 20 percent of the nitrate level, since these two ions elute very close together on the S_1 column being used for the halide analysis. The nitrate levels were estimated to be as much as 50 mg/L in the digests prepared using the Schoeniger flask procedure. Since a concentrated nitrate wash of the charcoal is prescribed in Interim Method 450.1 used for sample preparation to remove inorganic chloride, a modification to the sample washing procedure in that method is necessary if bromide is to be determined using the IC procedure.

TABLE 3. HALIDE SPIKE RECOVERY RESULTS USING THE SCHOENIGER FLASK OXIDATION PROCEDURE AND THE ION CHROMATOGRAPHIC DETERMINATIVE TECHNIQUE

Sample Identification	Spike Level, µg Total Halide[a]	µg Chloride Found in Given Sample[b]						Percent Recovery[c]	
		Replicate 1	Replicate 2	Replicate 3	Average	SD	RSD %	Chloride Only	Total Halide
Method blank	0	50.8	41.2	--[d]	46.0	6.8	15	NA[e]	NA[e]
Low level spike	100	152	140	131	141	10.5	7.5	106	95
High level spike	500	460	510	470	480	26.5	5.5	96	87

(a) Spiked using 20 µg/µL halide spiking solution containing 90% chloride and 10% bromide.
(b) Bromide could not be determined due to high nitrate levels.
(c) Corrected for the average chloride amount from the two reagent blank determinations.
(d) Two replicates only for the method blank.
(e) Not applicable.

The results of the sample wrapping paper washing experiment are presented in Table 4 and indicate that only 32 percent of the halide could be removed using the nitrate washing solution used in Interim Method 450.1. These results indicated that a further reduction in the halide blank level would have to be achieved with the use of an alternate wrapping paper. Subsequent work with the Schoeniger flask procedure was performed using Whatman Grade 541 white paper which was ignited using a small strip of the black sample wrapping paper evaluated above.

The results of the experiment to evaluate the source of the high nitrate levels are shown in Table 5, and these data indicate that the nitrate that is present in the samples is derived from both the charcoal and the black wrapping paper. Nitrate was not found in either the reagent blank or the Whatman 541 filter paper digests.

The experiment to evaluate the effectiveness of hydrazine for reducing bromate ion to bromide showed that hydrazine was not effective. No significant amount of bromide was detected, even though the level of sodium bromate used in the experiment was 5,000 ppm, or 2,650 ppm as bromide. A second experiment using hydrazine sulfate at levels recommended in the method also failed to reduce bromate to bromide. The absorbing solution in the original ASTM Method is 2N in KOH rather than the 0.1N which was used in these studies. However, the 2N solution cannot be used in the IC determinative step without either neutralization or 10- to 20-fold dilution. A neutralization is not possible without encountering column overloading problems similar to those found during the IC analysis of sodium biphenyl reagent extracts (discussed below). For these reasons, the hydrazine sulfate reduction step was eliminated from the procedure.

The Schoeniger flask technique appears to be a very useful oxidation approach considering both the cost and time of analysis. The turn around time for a combustion is approximately one and one-half hour per sample using this technique. This time includes preparing the sample, burning it, allowing the flask to stand for one hour, and transferring the sample to a storage container. The glassware costs about $150 per flask, which includes the stopper and sample carrier. An infrared igniter can be purchased for

TABLE 4. EFFECT OF A POTASSIUM NITRATE WASH ON HALIDE LEVELS IN BLACK SAMPLE WRAPPING PAPER

Sample Identification	µg Halide in Given Replicate				Percent Halide Removed (a)
	Replicate 1	Replicate 2	Replicate 3	Average	
Unwashed paper	18.3	15.2	17.0	16.8	(c)
Washed paper	12.2	10.8	(b)	11.5	32

(a) $\frac{\text{Average µg, unwashed - Average µg, washed}}{\text{Average µg, unwashed}} \times 100.$

(b) Sample lost due to cell contamination.

(c) Not applicable.

TABLE 5. DETERMINATION OF CHLORIDE AND NITRATE LEVELS BY ION CHROMATOGRAPHY IN WRAPPING PAPER AND REAGENTS USED IN SCHOENIGER FLASK OXIDATION

Sample Identification[a]	µg Chloride in Given Replicate						µg Nitrate in Given Replicate					
	Rep. 1	Rep. 2	Rep. 3	Average	SD	RSD, %	Rep. 1	Rep. 2	Rep. 3	Average	SD	RSD, %
Reagent blank	10	--[b]	--	10	--	--	ND[d]	ND	ND	--	--	--
Whatman 541 paper	20	30	26	28	2.0	7.1	ND	ND	ND	--	--	--
Whatman 541 paper and 40 mg charcoal	34	26	26	29	4.6	16	130	150	150	140	11	8.1
Black wrapping paper and 40 mg charcoal	58	--[c]	--	58	--	--	230	--	--	230	--	--

(a) All samples prepared using new washing procedure described on page 9 of the text.
(b) Only one replicate for reagent blank. Statistics are not appropriate.
(c) Only one replicate for black wrapping paper and charcoal sample.
(d) Not detected. Statistics not appropriate.

about $100. Replacement flasks are about $20 for the 1-liter size. For an investment of about $1,000, a set of six flasks and an igniter can be acquired, and an analyst can easily perform 12 oxidations in a single working day. One limitation to this approach is the fact that the method has inherently high background halide levels (approximately 20 µg/determination) which limit the usefulness of this approach to halide levels above 0.2 mg/L, assuming a 100 mL sample size.

Evaluation of the Parr Bomb Oxidation Procedure

The results for method blanks and charcoal spiked at the 100 µg halide level are presented in Table 6 and show very poor recovery for chloride. Although the charcoal method blanks are significantly lower than those obtained using the Schoeniger flask technique, the bomb oxidation procedure appears to be unsuitable in its present form due to the low recoveries for chloride. As discussed above for the Schoeniger flask method, nitrate levels were very high, and prevented the quantification of bromide by IC in the samples. In the case of the oxygen bomb sample preparation, the high nitrate levels are believed to be a result of using a 1 percent solution of collodion in amyl acetate as a combustion accelerator. Collodion is a nitrocellulose preparation and is a standard accelerator used in bomb combustion work. It was not possible to fire the charcoal without it.

The results of the 500 µg spike recovery using the Parr bomb oxidation technique and one-hour absorption time are shown in Table 7. Although the average recovery of 23 percent chloride is much higher than the 4 percent obtained at the 100 µg level using only a 15-minute absorption time, these data indicate that the Parr bomb technique is unsuitable as an oxidation approach for charcoal.

The main difficulty with the Parr bomb technique appears to be incomplete combustion of the charcoal used in the Dohrmann adsorption module. In all samples produced by this method, a portion of the charcoal was present that has not been burned, which accounts for the low recoveries obtained. Apparently the ignition and burning of the sample was so rapid that some of the charcoal was blown out of the quartz cup before it has had a chance to

TABLE 6. HALIDE SPIKE RECOVERY RESULTS OBTAINED USING THE COMBUSTION BOMB OXIDATION PROCEDURE AND THE ION CHROMATOGRAPHIC DETERMINATIVE TECHNIQUE

Sample Identification	Spike Level, µg Total Halide[a]	µg Chloride Found in Given Replicate						Percent Recovery	
		Replicate 1	Replicate 2	Replicate 3	Average	SD	RSD, %	Chloride Only	Total Halide
Method blank (without quartz collector)	0	35	32	(b)	34	2.1	6.3	NA[c]	NA
Method blank	0	14	16	16	15	1.2	7.5	NA	NA
Spiked charcoal	100	16	22	18	19	3.1	16	4.4	4

(a) Spiked using a 20 µg/µL halide spiking solution containing 90% as chloride and 10% as bromide.
(b) Two replicates only for blank determinations without quartz collector.
(c) Not applicable.

TABLE 7. HALIDE SPIKE RECOVERY RESULTS OBTAINED USING THE COMBUSTION BOMB OXIDATION PROCEDURE WITH ONE HOUR ABSORPTION TIMES AND THE ION CHROMATOGRAPHIC DETERMINATIVE TECHNIQUE

Sample Identification	Spike Level, µg Total Halide	µg Chloride Found in Given Replicate					RSD, %	Percent Recovery	
		Replicate 1	Replicate 2	Replicate 3	Average	SD		Chloride Only	Total Halide
Method blank	0	16	--[b]	--[b]	16	--	--	(c)	(c)
Spiked charcoal	500[a]	98	90	170	120	44	37	23	21

(a) Spiked using a 20 µg/µL halide spiking solution. Chloride was present at a level of 450 µg, and bromide at 50 µg.
(b) Dash indicates not determined. Only one blank level determination was made.
(c) Not applicable.

burn. This incomplete combustion which was typical with the charcoal samples has also been observed with coal samples oxidized using the Parr bomb procedure.

The oxygen bomb technique does not appear to be suitable for use in determining organic halide. Although the blank values are much lower than those for the Schoeniger flask technique, recoveries are very poor. An oxygen bomb can be purchased for approximately $700.00, excluding the cost of a quartz insert. The turn around time for a combustion experiment is approximately two hours assuming one hour absorption time. Taking into account the time required to clean and dry the apparatus between runs, an analyst can perform only three to four combustions in a single working day if only one bomb is available.

Evaluation of the Sodium Biphenyl Reagent Procedure

Due to the inability to analyze sodium biphenyl extracts by ion chromatography because of high nitrate concentrations and interferences encountered in the chloride ion specific electrode determinative technique, all samples prepared with this reagent were analyzed using the ASTM D-512 colorimetric chloride procedure.

The results obtained from blank and spiked samples prepared both with and without charcoal using the sodium biphenyl method are presented in Table 8. The data from the samples prepared without charcoal show a blank halide level of 60 to 70 μg halide per vial of sodium biphenyl solution and a spike recovery of 100 percent. Those samples prepared using the granulated activated charcoal show a blank level of 68 to 88 μg halide per vial of reagent and a recovery of 170 percent.

The introduction of charcoal to the reagent resulted in several difficulties. The first problem with this technique is that the charcoal tends to be carried over into the aqueous extract during separation. This necessitated an additional filtration step after the extraction of the sample, which was not necessary on samples that did not contain solids. The reason for the high recovery of halide was not determined and is difficult to explain. Since the method blank samples were treated in the same manner, the

TABLE 8. HALIDE SPIKE RECOVERY RESULTS OBTAINED USING THE SODIUM BIPHENYL SAMPLE PREPARATION PROCEDURE AND THE ASTM D512 COLORIMETRIC METHOD

Sample Identification	Spike Level, µg Total Halide	µg Halide Found in Given Replicate					R.S.D. (%)	Average Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average	S.D.		
Method Blank Without Charcoal	0	70	62	62	65	4.6	7.1	NA[a]
Spiked Sample Without Charcoal	500	580	540	640	580	50	8.6	100
Method Blank With Charcoal	0	68	88	72	76	11	14	NA
Spiked Charcoal	200	410	400	410	410	6.9	1.7	170

(a) Not applicable.

high results do not appear to be a result of bound chloride in the charcoal. One possible explanation lies in the fact that the spiked charcoal samples were air dried prior to preparation. This step was necessary in order to allow time for the methanol carrier solution to evaporate, but could possibly have resulted in a small amount of organic chloride from the air being adsorbed, even though the samples were prepared in a room in which no halogenated solvents are present.

These results indicate that additional work is necessary to evaluate the high recoveries of spikes on charcoal. However, the sodium biphenyl method is less desirable than the Schoeniger flask method for the preparation of adsorption charcoal samples for several reasons. The blank levels are in the range of 60 to 80 µg halide in the reagent, as shown in Table 8. Blank results obtained using the Schoeniger flask method have been as low as 35 to 40 µg using a single sheet of the black sample wrapping paper and were found to be less than 30 µg for samples prepared using the Whatman filter paper. In addition, a sample volume for the extract of 25 mL is the minimum volume attainable with the sodium biphenyl approach when using three extractions. The volume of the sample prepared using the Schoeniger flask procedure is 10 mL and could possibly be reduced to 5.0 mL if necessary. The combination of these two parameters leads to a lower detection limit for the Schoeniger flask method.

The results of halide recovery from spiked reagent water using the sodium biphenyl species generation approach and colorimetric chloride determination are shown in Table 9. Recovery from spiked charcoal averaged 90 percent with a relative standard deviation of 3.3 percent. The average recovery from charcoal prepared using spiked reagent water and the adsorption procedure from Interim Method 450.1 was 72 percent with a relative standard deviation of 25 percent.

The higher recovery for spiked charcoal indicates possible losses of halide in the sample preparation and adsorption steps. This is conceivable since the spiking solution used in these experiments contains two purgeable compounds, even though extreme care was exercised in the preparation of the aqueous solutions for the adsorption module preparation. One possible point

TABLE 9. HALIDE SPIKE RECOVERY RESULTS FOR REAGENT WATER SAMPLES OBTAINED USING THE SODIUM BIPHENYL SPECIES GENERATION APPROACH AND THE COLORIMETRIC CHLORIDE METHOD

Sample Identification	Spike Level[a] Total Halide, mg/L	Total Halide as Chloride in Given Replicate, mg/L				Standard Deviation	RSD, %	Average Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average			
Charcoal Method blank	0.00	0.68	0.72	--[b]	0.70	0.028	4.0	NA[c]
Spiked Charcoal[d]	5.00	5.10	5.40	5.10	5.20	0.17	3.3	90
Spiked Reagent Water	5.00	3.10	5.20	4.60	4.30	1.10	25	72

(a) Water samples and charcoal spiked with a 20 µg/µL halide spike solution.
(b) Only two replicate analyzed.
(c) NA = not applicable
(d) Spiked charcoal was not processed using the adsorption module procedure of the other samples.

where purgeable components were lost was in the sample transfer to the adsorption module reservoir. In the transfer, the sample is aerated when poured into the reservoir, which could lead to losses since there is a relatively large headspace in the reservoir.

One other possible explanation for lower recoveries may be in the reaction step in which damp charcoal is placed in with the sodium biphenyl reagent. A coating of reaction product on the charcoal surface may possibly reduce the reaction efficiency since a small amount of the reagent will react with water at the charcoal surface.

The most difficult part of the sodium biphenyl method for charcoal sample is in the extraction step. During extraction, the three phases present in the separatory funnel combine to form an emulsion that prevents efficient separation of the aqueous and organic layers. Large globs of charcoal, water, and organic layer combine in the aqueous layer, preventing the removal of the lower aqueous phase without carryover of charcoal and spent reagent. This results in a very heterogeneous extract that must be extracted again with toluene to remove most of the spent organic reagent and finally filtered to remove charcoal particulates before proceeding with the colorimetric analysis. These extra sample processing steps result in a more complex procedure that requires extra time and increases the chances of contamination.

The principal advantage to the sodium biphenyl method is the cost. Enough reagent can be purchased for about $20.00 to do 20 samples, excluding the cost of the separatory funnels or glassware associated with the procedure. However, a consideration of the lower recovery and higher blank levels than those obtained using the Schoeniger flask method, as well as the increased operator time necessary to cope with a difficult separation problem and additional sample processing steps far outweigh any cost advantage of this approach. Therefore, the recommendation is made that this method be excluded from further consideration for the preparation of charcoal samples for groundwater organic halide determinations.

TASK 2: EVALUATION OF THE DETERMINATIVE TECHNIQUE

Evaluation of IC as the Determinative Technique

Plots of the calibration curves for the low and high range calibration of chloride using the S_2 column are presented in Figures 1 and 2, and the linear regression analysis parameters are shown on the figures. The low level curve exhibits a small positive bias at zero concentration due to a chloride background level of approximately 0.06 µg/mL in the dilution water. The S_2 column was not evaluated further due to the better separation of bromide and nitrate ions on the S_1 column. Calibration curves obtained using the S_1 column are presented in Figures 3 and 4 for chloride and bromide over the range of 0.0 to 10 µg/mL. These calibration curves show good linearity over the ranges tested. The sensitivity for chloride is approximately five times that of bromide based upon peak height comparisons, which is a direct consequence of the elution order of the two analytes. As shown in Figure 5, chloride elutes at approximately five minutes on the S_1 column under the conditions evaluated, while bromide elutes at 14 minutes and shows a broader peak. Because of this broadening, the detection limit for bromide is much higher than that for chloride, and is estimated to be about 0.5 µg/mL, compared to about 0.05 µg/mL for chloride. The separation of six common anions is illustrated in Figure 6, for the S_1 column. As shown in the figure, bromide and nitrate ions are only partially resolved and as a result of this incomplete separation, small quantities of one of these ions could not be determined in the presence of large amounts of the other. This condition exists for bromide determinations in extracts from charcoal used in groundwater analysis where a nitrate wash has been used to remove inorganic halide from the charcoal. The nitrate obscures small amounts of bromide and renders IC ineffective for halide speciation when applied to samples prepared using the Interim Method 450.1 adsorption method for total organic halides. Figure 7 shows a chromatogram of a spiked charcoal sample prepared using the Schoeniger flask oxidation method and the effect of the high nitrate levels on bromide-nitrate separation. The sample contained 5 µg/mL bromide.

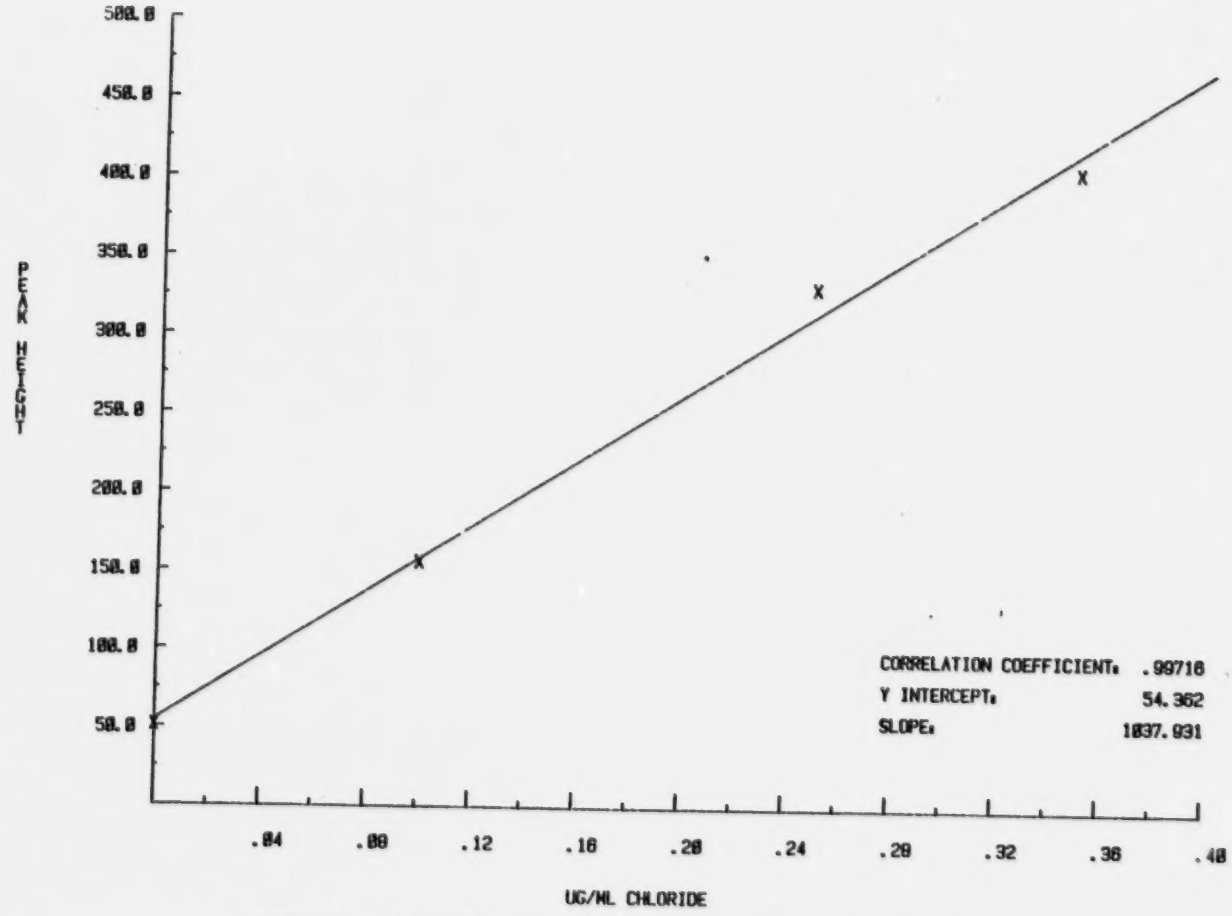

FIGURE 1. CALIBRATION CURVE FOR THE ION CHROMATOGRAPHIC DETERMINATION OF CHLORIDE FROM 0.0 to 0.35 μg/mL USING THE S_2 COLUMN.

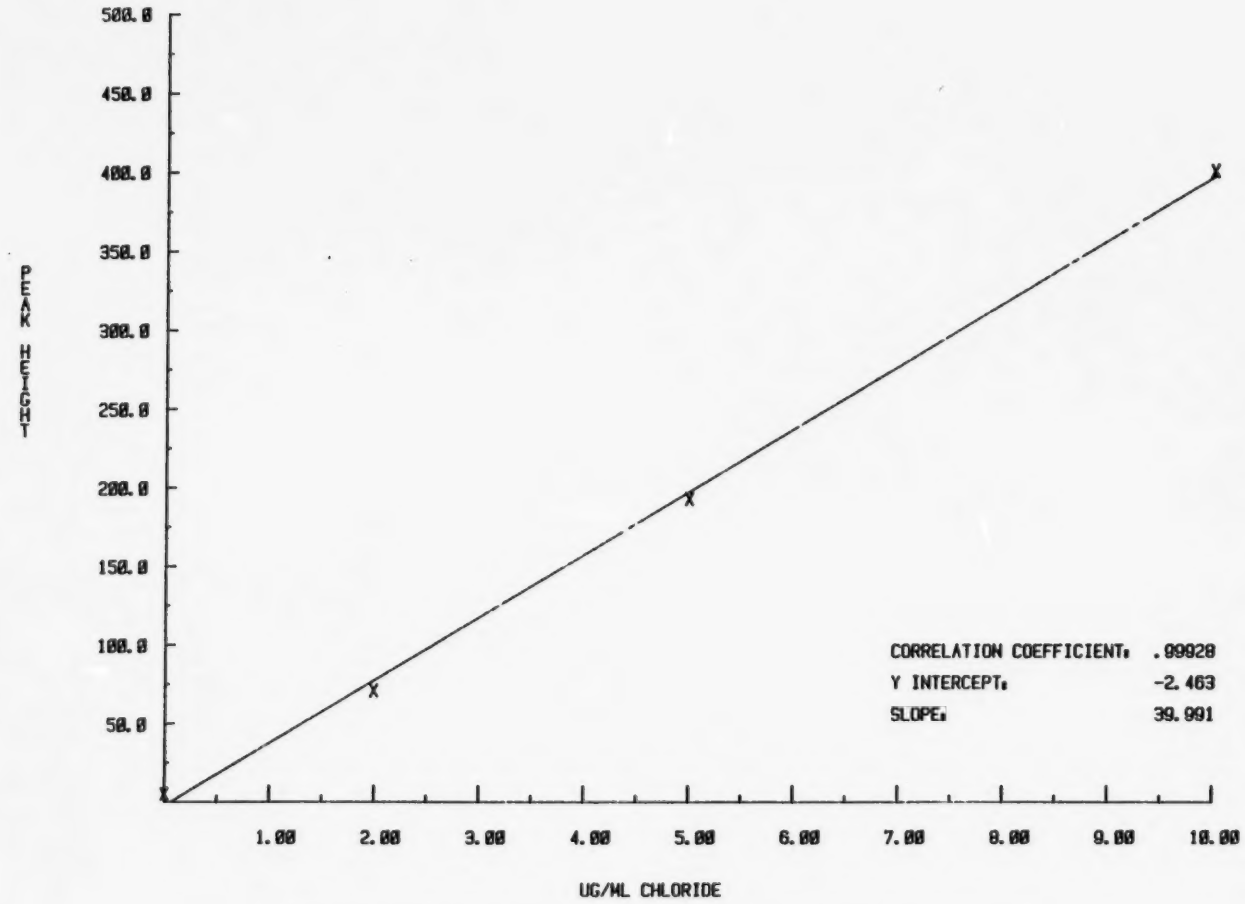

FIGURE 2. CALIBRATION CURVE FOR THE ION CHROMATOGRAPHIC DETERMINATION OF CHLORIDE FROM 0.0 to 10.0 µg/mL USING THE S_2 COLUMN.

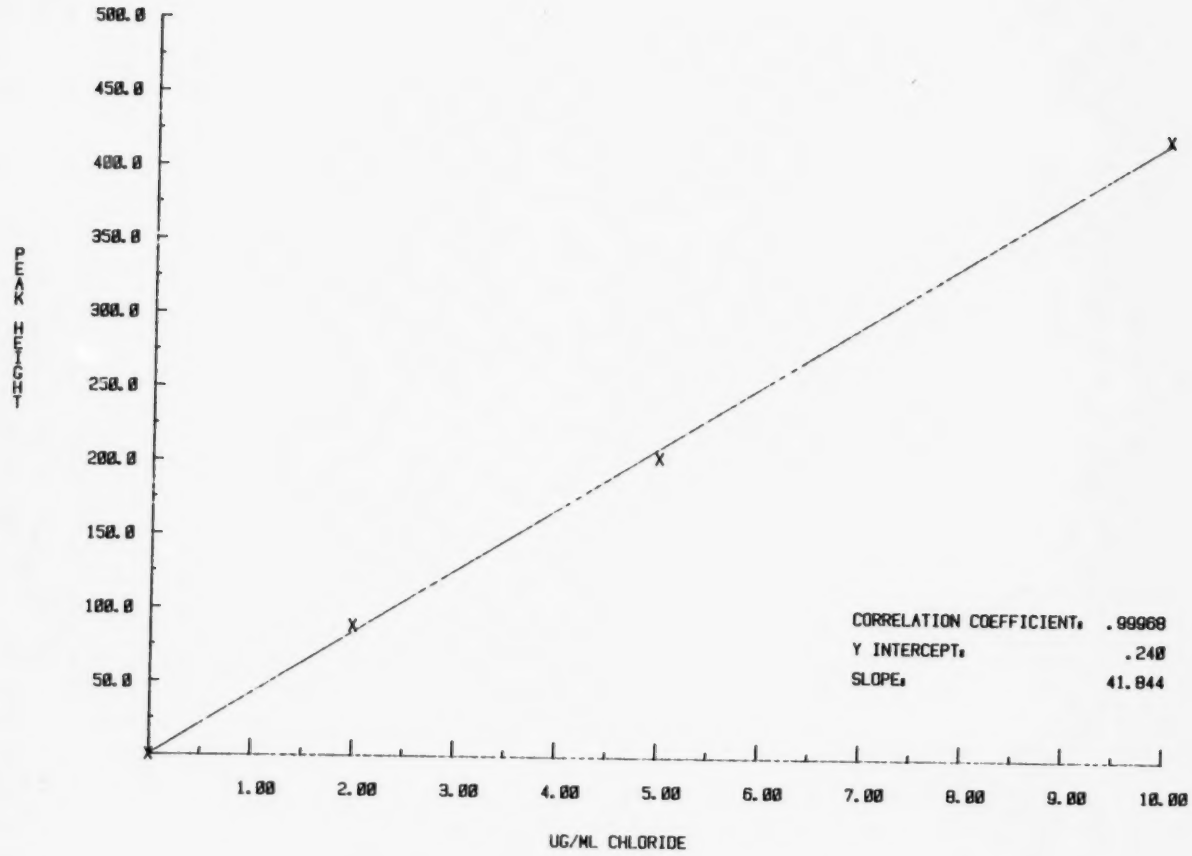

FIGURE 3. CALIBRATION CURVE FOR THE ION CHROMATOGRAPHIC DETERMINATION OF CHLORIDE FROM 0.0 to 10 µg/mL OBTAINED USING THE S_1 COLUMN.

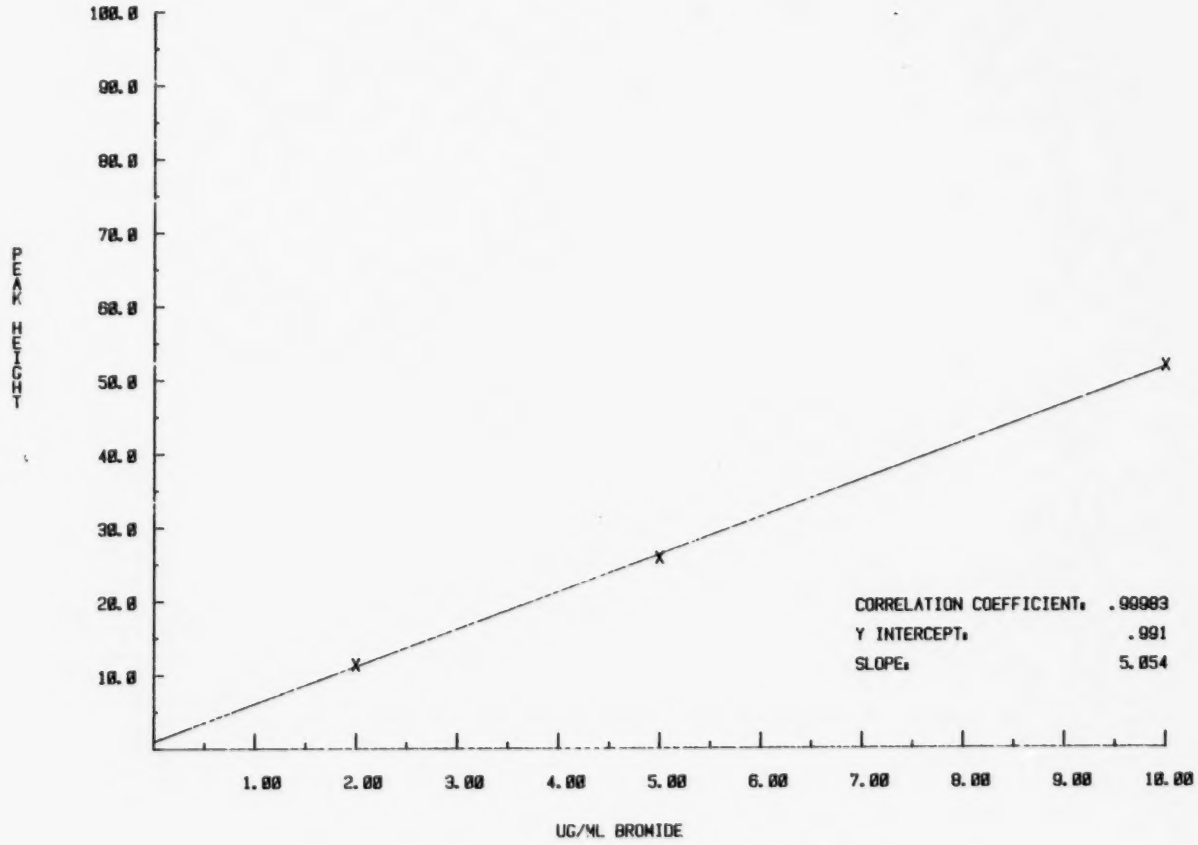

FIGURE 4. CALIBRATION CURVE FOR THE ION CHROMATOGRAPHIC DETERMINATION OF BROMIDE FROM 0.0 to 10 ug/mL OBTAINED USING THE S_1 COLUMN.

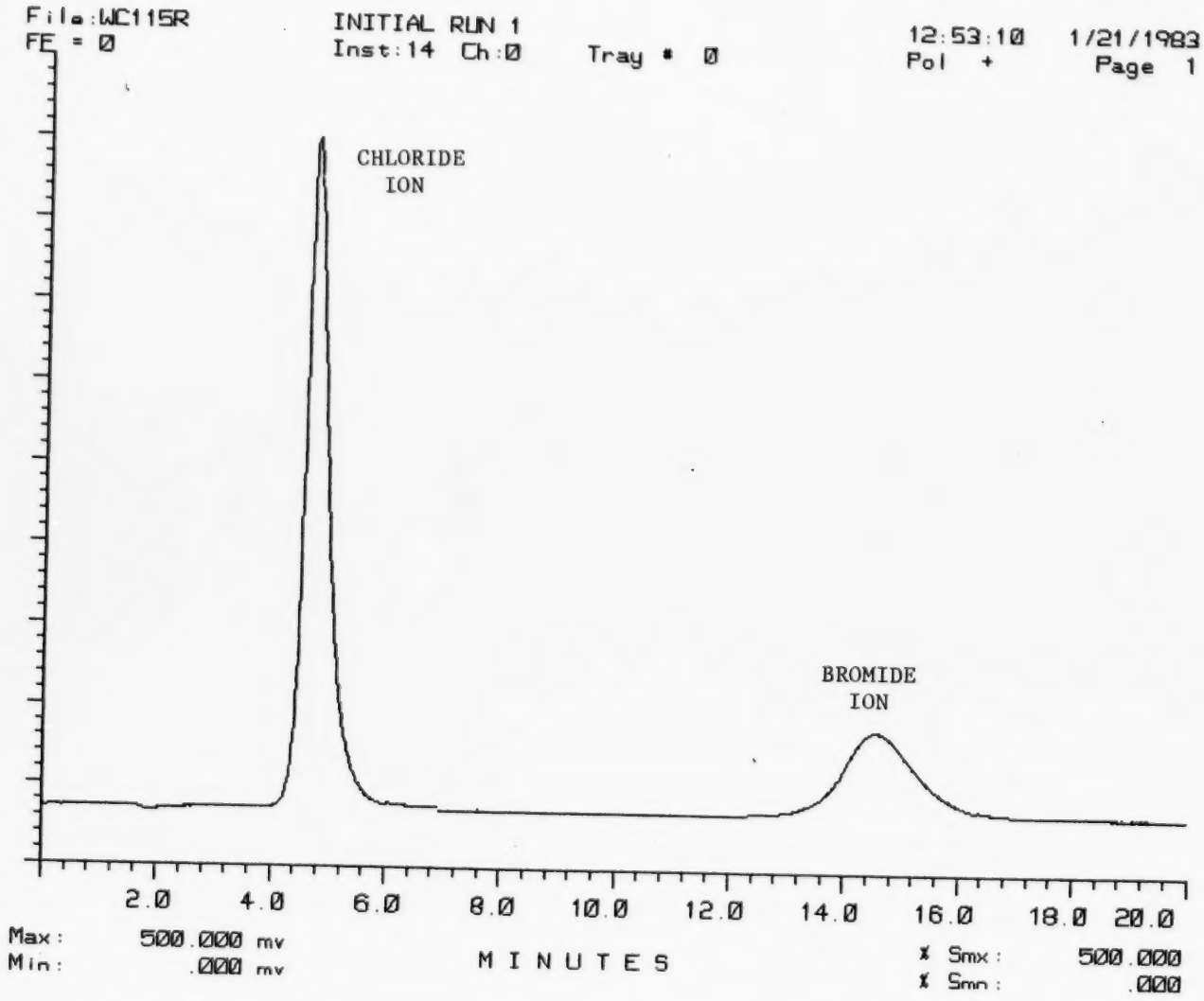

FIGURE 5. ION CHROMATOGRAM OBTAINED USING THE S_1 COLUMN SHOWING THE RELATIVE RESPONSE FOR 10 µg/mL CONCENTRATIONS OF CHLORIDE AND BROMIDE.

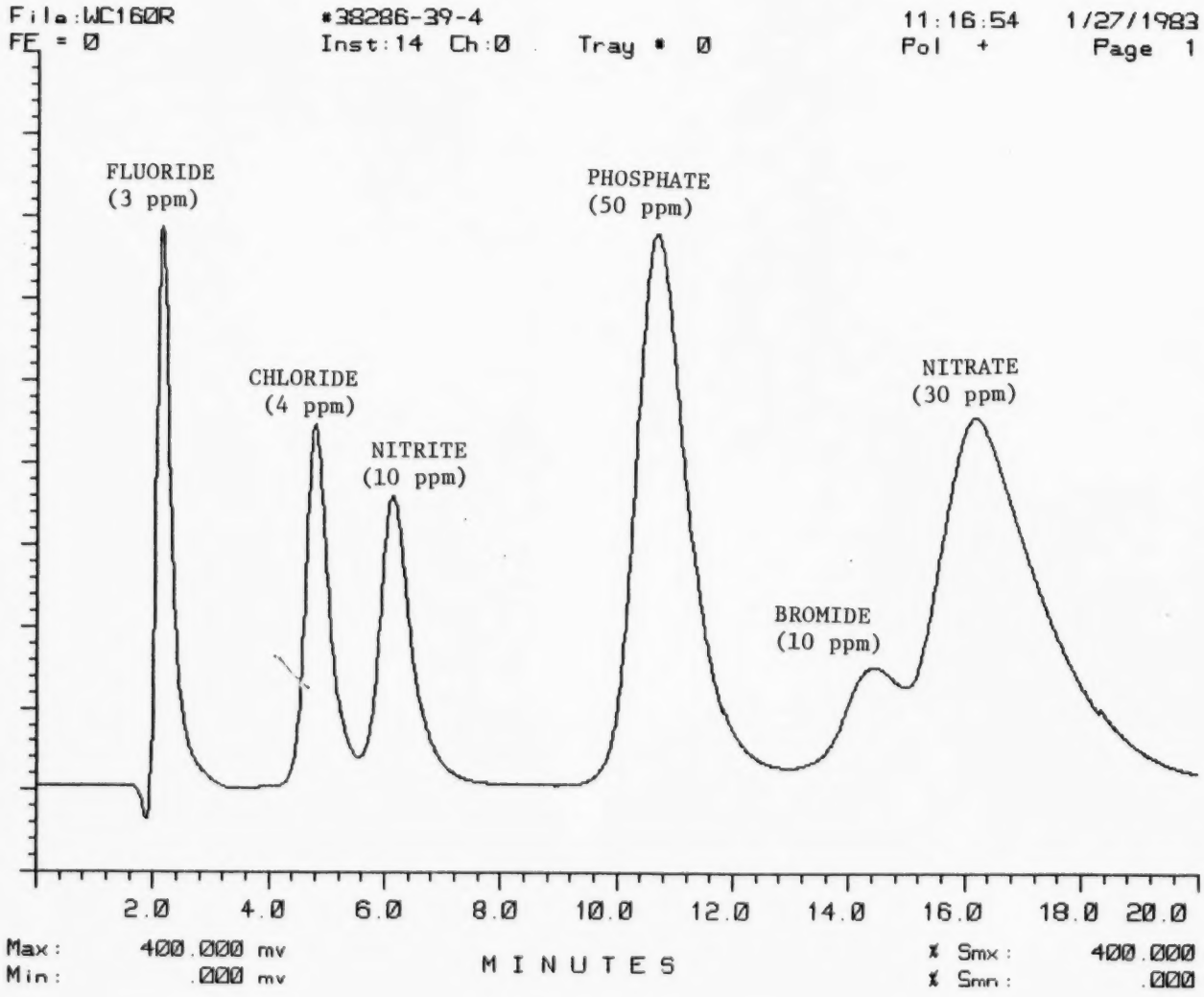

FIGURE 6. IC SEPARATION OF SIX ANIONS ON THE S_1 COLUMN.

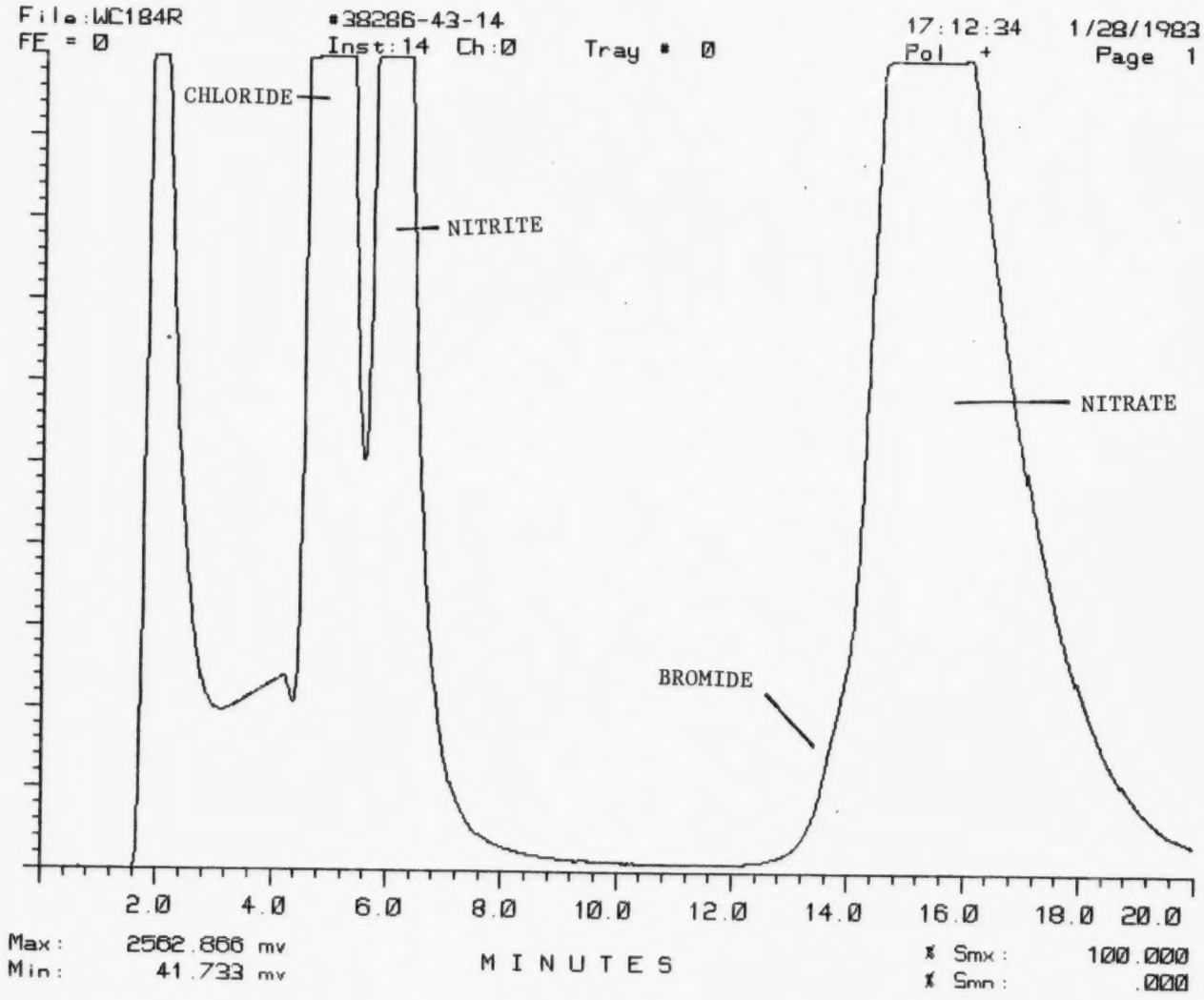

FIGURE 7. ION CHROMATOGRAM OBTAINED USING THE S_1 COLUMN OF A 500 µg HALIDE SPIKE SAMPLE PREPARED USING THE SCHOENIGER FLASK METHOD.

Evaluation of the ISE as the Determinative Technique

The calibration curve data for chloride ion determination by ISE presented in Figure 8 and in Table 10 show only a small response difference of 4 mV for calibration standards of 1 and 4 µg/mL. These data indicate that 1 µg/mL is very close to the detection limit for the chloride electrode. The response for low bromide levels is similar and the detection limits for bromide is also about 1 µg/mL. The data in Table 10 also show almost equivalent response for bromide using the chloride electrode at the 10 µg/mL level. At the 100 µg/mL bromide ion level, the bromide response is equivalent to 65 µg/mL of chloride ion. These results indicate that the chloride ISE is useful for halide determinations at levels above 1 µg/mL. Since the response to bromide and chloride is so similar, this determinative technique should give adequate results for TOX in samples containing both chloride and bromide and for which digestion does not give interferring species.

The results of the analysis of method blank and spiked samples from the Schoeniger flask oxidation procedure using the ISE are shown in Table 11. These data indicate a high positive interference in the samples which results in apparent recoveries of 240 percent for the 500 µg spike level and 380 percent for the 100 µg spike. The ISE results are compared with the IC results for the same samples in Table 12.

In order to determine if the samples had absorbed chloride from the container or had become contaminated with chloride, one replicate each from the 100 µg and 500 µg spiked samples was reanalyzed by IC. The IC results showed the 100 µg spiked sample to contain 125 µg chloride and the 500 µg spiked sample to contain 450 µg chloride. These results compare well with the original results shown in Table 12 for the IC analyses indicating that the samples were not contaminated during storage. As a further check, the 4 and 10 µg/mL standards used for ISE calibration were analyzed by IC and found to contain 3.8 and 9.4 µg/mL for chloride, respectively.

These results show that the chloride ISE is not suitable for halide determination in Schoeniger flask digestates because of the high positive

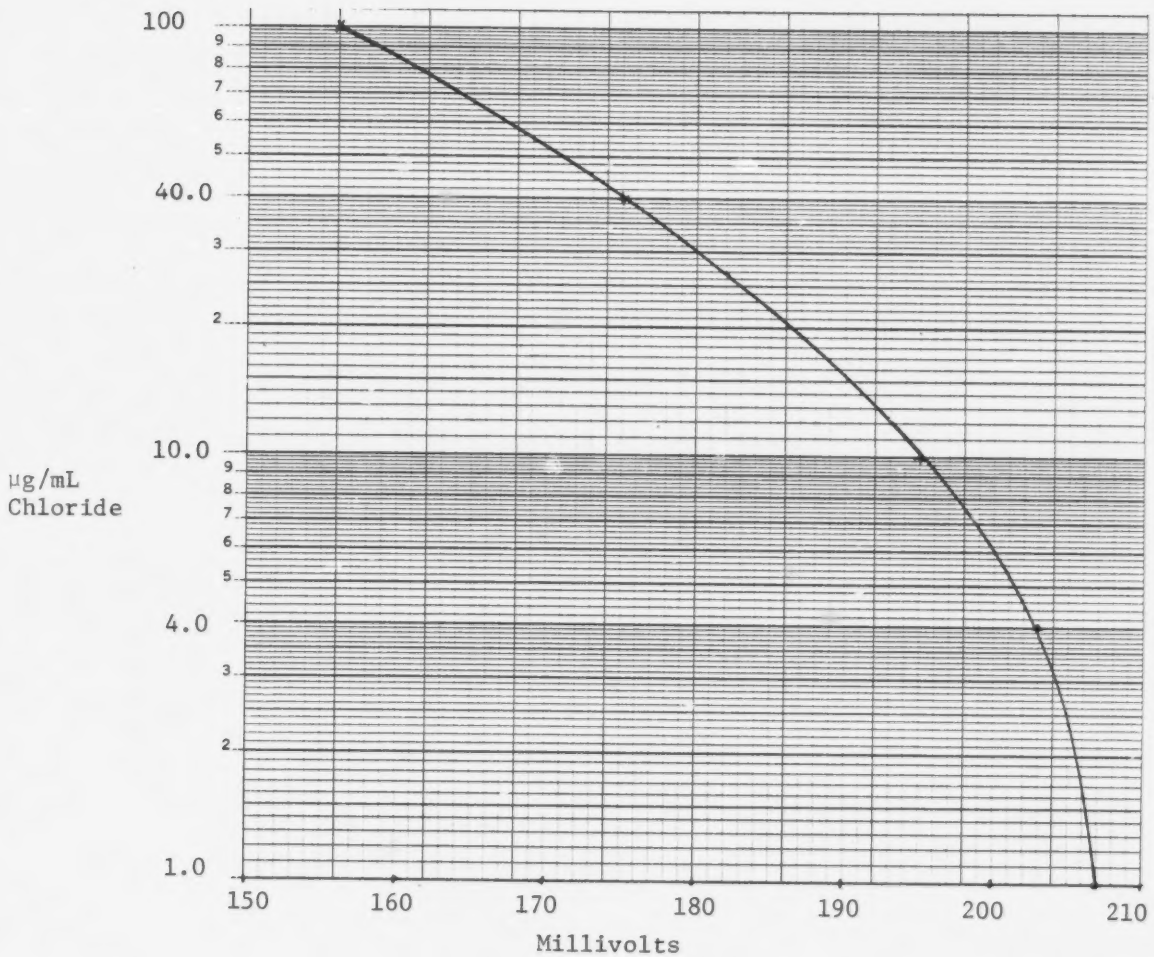

FIGURE 8. CALIBRATION CURVE FROM 1.0 TO 100 µg/mL CHLORIDE OBTAINED USING THE CHLORIDE ION SPECIFIC ELECTRODE.

TABLE 10. CALIBRATION CURVE DATA FOR CHLORIDE AND BROMIDE IONS USING THE CHLORIDE ION SPECIFIC ELECTRODE

Calibration Level µg/mL	Millivolt Reading for Given Ion	
	Chloride	Bromide
1	207	218
4	203	ND[a]
10	195	197
40	175	ND
100	156	165

(a) Not determined.

TABLE 11. ANALYSIS OF BLANK AND SPIKED SAMPLES FROM SCHOENIGER FLASK OXIDATION USING THE ION SELECTIVE ELECTRODE

Sample Identification	Spike Level, µg Halide	µg Halide Found in Given Replicate				SD	RSD, %	Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average			
Reagent blank	0	10	20	ND[a]	15	7.1	47	NA[b]
Low level spike	100	370	370	460	400	52	13	380
High level spike	500	1300	1200	1000	1200	150	13	240

(a) Only two replicate determinations made for reagent blank.
(b) Not applicable.

TABLE 12. COMPARISON OF RESULTS FROM ION SELECTIVE ELECTRODE AND ION CHROMATOGRAPHY FOR BLANK AND SPIKED SAMPLES FROM SCHOENIGER FLASK OXIDATION

Sample Identification	Spike Level, µg Halide	Average µg Halide Found For Given Method		Average Percent Recovery for Given Method[a]	
		Ion Selective Electrode	Ion Chromatography	Ion Selective Electrode	Ion Chromatography[b]
Reagent blank	0	15	46	NA	NA
Low level spike	100	400	141	380	95
High level spike	500	1200	480	240	87

(a) Corrected for reagent blank and based on total amount of halide spiked.
(b) Chloride ion only determined using ion chromatography.

interference. No explanation is apparent for the relatively low reagent blank reading obtained.

Evaluation of the ASTM D-512 Colorimetric Chloride Determinative Technique

Linearity of Response and Detection Limit Studies--

The absorbances of solutions containing chloride, bromide, and nitrite concentrations ranging from 0 to 100 µg/mL are shown in Table 13 for analyses using the ASTM D-512 Colorimetric method. These data show that bromide ion responds similarly to chloride, and that no significant response versus concentration, was obtained for nitrite ion. A calibration curve for chloride ion from 1 to 20 µg/mL is shown in Figure 9. This curve shows that the linear region is from 1 to 4 µg/mL and that the response is no longer linear after 4 µg/mL on the Spectronic 21 spectrophotometer. The average blank level for reagents was found to be 0.026 absorbance units. This result places the detection limit using the colorimetric method at about 0.5 µg/mL when a 1.0 cm path length cell is employed.

The results of the experiment to characterize the nitrite interference listed in the colorimetric method are shown in Table 14. These data show only a slight increase in the chloride response when 100 µg/mL of nitrite is present in the sample and could possibly be a result of a small amount of chloride contamination in the nitrite standards. These results indicate that the nitrite levels present in the Schoeniger flask digest, which are estimated to be about 100 µg/mL for the IC analyses of these samples, will not cause a significant interference in the chloride results.

Spiked Charcoal Sample Analyses--

The results of the colorimetric determinations of chloride in the blank and spiked Schoeniger flask samples are presented in Table 15. Although the recovery for chloride was only 66 percent for the experiment where only chloride (as 2,4,6-trichlorophenol) was spiked, those extracts were prepared when the procedure called for the use of two pieces of black wrapping paper. This resulted in a large reagent blank, and the spiked samples had an absorbance reading only twice the blank level. The other data points were

TABLE 13. COMPARISON OF ABSORBANCE OF CHLORIDE, BROMIDE, AND NITRITE CALIBRATION CURVES IN ASTM D-512 COLORIMETRIC METHOD

Calibration Level, µg/mL	Absorbance Reading for Given Analyte		
	Chloride	Bromide	Nitrite
0	0.026	0.026	0.026
1	0.065	0.048	0.032
4	0.174	ND[a]	ND
10	0.335	0.281	0.030
40	0.737	1.035	0.028
100	1.147	ND	0.037

(a) Not determined.

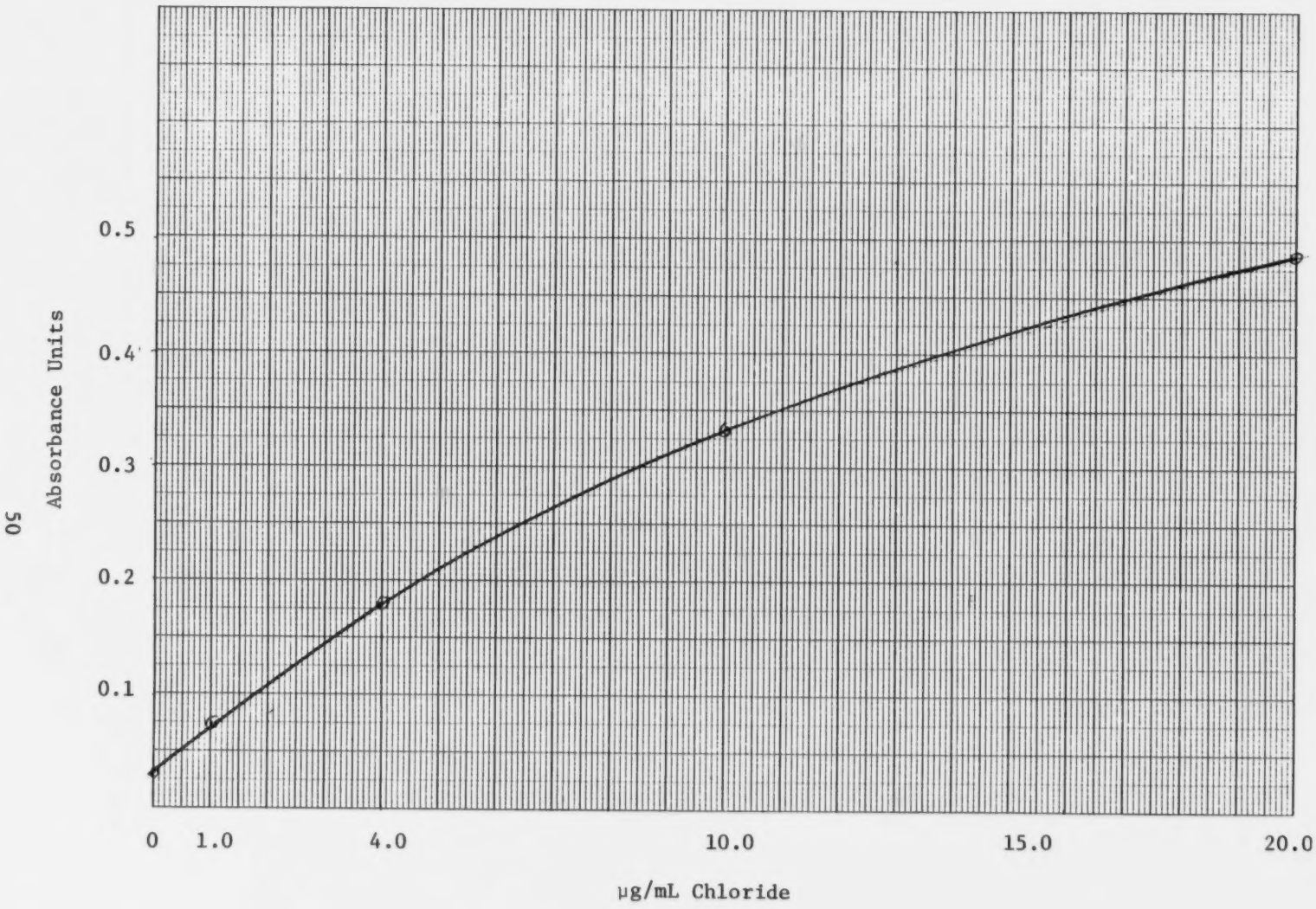

FIGURE 9. CALIBRATION CURVE FOR CHLORIDE OBTAINED USING COLORIMETRIC METHOD.

TABLE 14. EFFECT OF NITRITE ON CHLORIDE ABSORBANCE IN THE ASTM D-512 COLORIMETRIC METHOD FOR CHLORIDE

Sample Identification	Absorbance Reading of Given Replicate					RSD, %
	Replicate 1	Replicate 2	Replicate 3	Average	SD	
10 µg/mL chloride	0.323	0.325	0.323	0.324	0.0012	0.36
10 µg/mL chloride and 100 µg/mL nitrite	0.327	0.332	0.332	0.330	0.0029	0.87

TABLE 15. HALIDE SPIKE RECOVERY RESULTS OBTAINED USING THE SCHOENIGER FLASK OXIDATION PROCEDURE AND THE ASTM D512 COLORIMETRIC METHOD

Identification	Spike Level, µg	µg As Chloride Found in Given Replicate				S.D.	R.S.D. (%)	Average Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average			
Method Blank (2 Sheets of Black Paper)	0	64	67	(a)	66	2.1	3.2	(b)
Chloride Spike (2 Sheets of Black Paper)	100(c)	130	130	140	130	5.5	4.2	64
Method Blank (1 Sheet of Black Paper	0	37	36	(a)	36	0.71	1.9	(b)
Low Level Halide Spike (1 Sheet of Black Paper)	100(d)	140	140	130	140	5.5	4.0	104
Higher Level Halide Spike (1 Sheet of Black Paper)	500(d)	480	520	530	510	30	6.0	99

(a) Only two replicates available.
(b) Not applicable.
(c) Spiked with 5.0 µL of a 20 µg/µL as halide stock derived from 2,4,6-trichlorophenol.
(d) Spiked using the 20 µg/µL three component halide stock described on page 5 of the text.

obtained from the experiment in which only one piece of black wrapping paper and the three component spike solution were used. A lower blank level, good precision, and 100 percent recovery at both the 100 and 500 μg halide spike level were obtained in these experiments. These data indicate that the colorimetric method is adequate for measuring halide levels in the Schoeniger flask extracts.

A comparison of the results of halide analyses on the same sample sets by ISE, IC, and the ASTM colorimetric method is shown in Table 16. The excellent agreement between the latter two methods indicates that there is no advantage to using IC for these analyses. In light of other data which show that speciation of chloride and bromide ions is not possible with IC due to high nitrate levels in the charcoal, the colorimetric procedure has been selected as the recommended method for all subsequent work. The use of the more expensive IC procedure should only be used where high levels of interferences are suspected or for confirmation of halide values in this type of sample matrix. The colorimetric procedure has also been found to be the only one of those evaluated which gives reasonable results with the sodium biphenyl reagent method.

Analysis of Samples Prepared Using Interim Method 450.1 Adsorption Procedure--

The results of halide spike recoveries from spiked reagent water, domestic well water, and monitoring well water, prepared using the charcoal adsorption procedure from Interim Method 450.1 and the Schoeniger flask/colorimetric chloride method, are presented in Table 17. The results for the Dohrmann microcoulometric detector analysis of equivalent samples are presented in Table 18.

The data from Table 17 show the excellent precision and recovery of the Schoeniger flask/colorimetric method approach for spiked water samples prepared using the charcoal adsorption method. This method was found to give better recovery and precision than the Dohrmann microcoulometric method (Table 18) at the spike levels evaluated in these experiments. It should be noted here that the reagent method blank and unspiked water samples

TABLE 16. COMPARISON OF RESULTS OF HALIDE RECOVERIES IN SAMPLES GENERATED WITH THE SCHOENIGER FLASK OXIDATION PROCEDURE AND ANALYZED WITH THREE DIFFERENT DETERMINATIVE TECHNIQUES

Sample Identification	Spike Level, µg Halide[b]	Average µg Halide Found For Given Method[a]			Average Percent Recovery For Given Method[a]		
		Ion Selective Electrode	Ion Chromatography	ASTM D-512 Colorimetric	Ion Selective Electrode	Ion Chromatography	ASTM D-512 Colorimetric
Reagent Blank	0	15	46	36	NA[c]	NA	NA
Low Level Spike	100	400	140	140	380	94	104
High Level Spike	500	1200	480	510	240	93	95

(a) Average of three determinations.
(b) Spiked with a 20 µg/µL halide solution containing 90% of the halide as chloride and 10% as bromide.
(c) NA = Not applicable.

TABLE 17. HALIDE SPIKE RECOVERY RESULTS FOR REAGENT WATER, DOMESTIC WELL WATER, AND MONITORING WELL WATER OBTAINED USING THE SCHOENIGER FLASK OXIDATION APPROACH AND THE COLORIMETRIC CHLORIDE METHOD

Sample Identification	Spike Level[a] Total Halide, mg/L	Total Halide as Chloride in Given Replicate, mg/L				Standard Deviation	RSD, %	Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average			
Unspiked Reagent Water Method Blank	0.00	0.18	0.15	0.28	0.20	0.068	33	NA[b]
Spiked Reagent Water	0.50	0.67	0.74	0.65	0.69	0.047	6.9	98
Unspiked Domestic Well Water	0.00	0.13	0.18	0.10	0.14	0.04	30	(b)
Spiked Domestic Well Water	5.0	5.20	4.90	5.30	5.10	0.20	3.9	99
Unspiked Monitoring Well Water	0.00	0.21	0.27	0.20	0.23	0.035	15	(b)
Spiked Monitoring Well Water	1.0	1.10	1.20	1.20	1.20	0.030	2.6	97

(a) Spiked with a 20 µg/µL halide solution containing 90% of the halide as chloride and 10% as bromide.
(b) NA = Not applicable.

TABLE 18. HALIDE SPIKE RECOVERY RESULTS FOR REAGENT WATER, DOMESTIC WELL WATER, AND MONITORING WELL WATER OBTAINED USING INTERIM METHOD 450.1

Sample Identification	Spike Level[a] Total Halide, mg/L	Total Halide in Given Replicate, mg/L				Standard Deviation	RSD, %	Average Percent Recovery
		Replicate 1	Replicate 2	Replicate 3	Average			
Reagent Water	0.00	0.028	--	--	0.028	--	--	NA[b]
Spiked Reagent Water	0.50	0.47	0.43	0.40	0.43	0.035	8.1	80
Domestic Well Water	0.00	0.023	0.028	(c)	0.026	0.0035	14	(b)
Spiked Domestic Well Water	5.00	4.50	4.50	4.50	4.50	0.023	0.5	90
Monitoring Well Water	0.00	0.068	0.062	0.073	0.068	0.0055	8.1	(b)
Spiked Monitoring Well Water	1.00	0.83	0.85	0.86	0.85	0.015	1.8	78

(a) Spiked with a 20 µg/mL halide solution containing 90% of the halide as chloride and 10% as bromide.
(b) NA = Not applicable.
(c) Only two replicates analyzed.

background halide levels differ considerably due to the high reagent blank values obtained using the Schoeniger flask/colorimetric halide method.

The results of the 50 µg halide spike and reagent water method blank indicate that the detection limit of this method is approximately 50 µg/100 mL of water, or 0.5 ppm, which is 2.5 times the average chloride blank level.

On the basis of these results, the recommendation is made to use the Schoeniger flask/colorimetric chloride method for the preparation and analysis of charcoal samples from the sample adsorption procedure from Interim Method 450.1.

TASK 3: METHOD VALIDATION

MDL for the Schoeniger Flask/Colorimetric TOX Method

The results of the MDL study for the Schoeniger flask/colorimetric TOX method using reagent water are presented in Table 19. An MDL of 0.15 mg/L was calculated for the method using a spike level of 0.51 mg/L of halide. The average recovery for the seven spiked replicates was 57 percent.

Method Validation Results for the Schoeniger Flask/Colorimetric TOX Method and EPA Method 9022, TOX by Neutron Activation Analysis

The results of the analyses of method validation samples by the Schoeniger flask/colorimetric TOX method, Interim Method 450.1, and EPA Method 9022 for chloride and bromide are presented in Tables 20 through 23, respectively. Interim Method 450.1, which uses the Dohrmann microcoulometric detector, was included for reference purposes. A summary of the results for each of the three methods is presented in Table 24 for direct comparison of the halide levels found.

The recoveries shown in Table 20 for the Schoeniger flask/colorimetric TOX method ranged from 56 percent for spiked reagent water to 105 percent for each of the groundwater samples. Precision of the method was good, with relative standard deviations for triplicate analyses of 11 percent or less in all cases.

TABLE 19. RESULTS OF METHOD DETECTION LIMIT STUDY FOR TOX METHOD USING SCHOENIGER FLASK COMBUSTION AND ASTM D-512 COLORIMETRIC HALIDE ANALYSIS

Sample Identification	Spike Level, mg/L	Amount of Halide Found in Given Replicate, mg/L										
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average[a]	SD	RSD, %	MDL
Reagent Water	Unspiked	0.18	0.15	0.28	0.20	0.18	--(b)	--(b)	0.20	0.049	25	--(c)
Reagent Water	0.51	0.43	0.50	0.50	0.43	0.49	0.57	0.49	0.49	0.048	9.8	0.15

(a) The average percent recovery for spiked reagent water was 57 percent.
(b) Only five replicates for unspiked reagent water.
(c) MDL not appropriate for unspiked sample.

TABLE 20. HALIDE SPIKE RECOVERY RESULTS FOR VALIDATION SAMPLES OBTAINED USING SCHOENIGER FLASK COMBUSTION AND ASTM D 512 COLORIMETRIC HALIDE ANALYSIS

Sample Identification	Spike Level, mg/L	Amount of Halide Found in Given Replicate, mg/L				SD	RSD %	Percent Recovery			
		Rep. 1	Rep. 2	Rep. 3	Average			Rep. 1	Rep. 2	Rep. 3	Average
Reagent water	Unspiked	0.20	0.18	--(a)	0.19	0.014	7.4	--(b)	--	--	--
Reagent water	0.51	0.43	0.50	0.50	0.48	0.040	8.5	47	61	61	56
Groundwater #1	Unspiked	0.22	0.24	0.23	0.23	0.010	4.3	--(b)	--	--	--
Groundwater #1	0.51	0.59	0.52	0.65	0.59	0.065	11	71	57	82	70
Groundwater #1	1.02	1.2	1.3	1.4	1.3	0.10	7.7	95	105	115	105
Groundwater #2	Unspiked	1.2	1.3	1.4	1.3	0.058	4.6	--(b)	--	--	--
Groundwater #2	5.1	4.2	4.1	4.4	4.2	0.15	3.6	57	55	61	58
Groundwater #2	10.2	8.1	8.3	7.4	7.9	0.47	6.0	67	69	60	65

(a) Sample lost.
(b) Not applicable.

TABLE 21. HALIDE SPIKE RECOVERY RESULTS FOR VALIDATION SAMPLES OBTAINED USING INTERIM METHOD 450.1

Sample Identification	Spike Level, mg/L	Amount of Halide Found in Given Replicate, mg/L				SD	RSD %	Percent Recovery			
		Rep. 1	Rep. 2	Rep. 3	Average			Rep. 1	Rep. 2	Rep. 3	Average
Reagent water	Unspiked	0.010	0.031	0.014	0.020[a]	0.0090	45	--[b]	--	--	--
Reagent water	0.50	0.47	0.43	0.40	0.43	0.035	8.1	88	80	75	81
Groundwater #1	Unspiked	0.035	0.045	0.053	0.044	0.009	20	--	--	--	--
Groundwater #1	0.51	0.62	0.57	0.49	0.56	0.065	12	106	96	80	94
Groundwater #1	1.0	1.5	1.2	1.1	1.3	0.21	17	130	120	110	120
Groundwater #2	Unspiked	1.7	1.9	1.5	1.7	0.22	13	--	--	--	--
Groundwater #2	5.1	3.5	4.0	4.5	4.0	0.52	13	35	45	55	45
Groundwater #2	10.2	8.7	7.4	8.6	8.2	0.69	8.4	69	56	68	64

(a) Additional blank levels of 0.018 mg/L and 0.029 mg/L were also averaged for the unspiked reagent grade water.
(b) Not applicable.

TABLE 22. CHLORIDE SPIKE RECOVERY RESULTS FOR VALIDATION SAMPLES OBTAINED USING METHOD 9022, TOTAL ORGANIC HALIDES (TOX) BY NEUTRON ACTIVATION ANALYSIS

Sample Identification	Spike Level, mg/L	Amount of Chloride Found in Given Replicate, mg/L				SD	RSD %	Percent Recovery			
		Rep. 1	Rep. 2	Rep. 3	Average			Rep. 1	Rep. 2	Rep. 3	Average
Reagent water	Unspiked	0.080	0.080	0.099	0.086	0.011	13	--(a)	--	--	--
Reagent water	0.46	0.43	0.45	0.45	0.44	0.012	2.6	75	79	79	78
Groundwater #1	Unspiked	0.13	0.11	0.096	0.11	0.017	15	--	--	--	--
Groundwater #1	0.46	0.52	0.54	0.53	0.53	0.010	1.9	89	93	91	91
Groundwater #1	0.92	1.4	1.3	1.4	1.4	0.058	4.2	140	130	140	140
Groundwater #2	Unspiked	3.0	2.7	2.5	2.7	0.25	9.2	--	--	--	--
Groundwater #2	4.6	6.8	6.8	6.5	6.7	0.17	2.3	89	89	83	87
Groundwater #2	9.2	10.0	8.0	9.9	9.3	1.1	12	79	58	78	72

(a) Not applicable.

TABLE 23. BROMIDE SPIKE RECOVERY RESULTS FOR VALIDATION SAMPLES OBTAINED USING METHOD 9022, TOTAL ORGANIC HALIDES (TOX) BY NEUTRON ACTIVATION ANALYSIS

Sample Identification	Spike Level, mg/L	Amount of Bromide Found in Given Replicate, mg/L				SD	RSD %	Percent Recovery			
		Rep. 1	Rep. 2	Rep. 3	Average			Rep. 1	Rep. 2	Rep. 3	Average
Reagent water	Unspiked	0.0011	0.0010	0.0011	0.0011	0.000058	5.4	--(a)	--	--	--
Reagent water	0.051	0.049	0.048	0.047	0.048	0.0010	2.1	94	92	90	92
Groundwater #1	Unspiked	0.0055	0.0054	0.0060	0.0056	0.00032	5.7	--	--	--	--
Groundwater #1	0.051	0.055	0.057	0.061	0.058	0.0031	5.3	100	107	102	103
Groundwater #1	0.102	0.099	0.096	0.100	0.098	0.0021	2.1	96	94	97	96
Groundwater #2	Unspiked	0.0060	0.0064	0.0088	0.0071	0.0015	21	--	--	--	--
Groundwater #2	0.51	0.43	0.47	0.50	0.47	0.040	8.5	83	91	97	90
Groundwater #2	1.02	0.89	0.52	0.91	0.77	0.22	28	87	50	89	75

(a) Not applicable.

TABLE 24. SUMMARY OF RECOVERY RESULTS FOR VALIDATION SAMPLES OBTAINED USING THE SCHOENIGER FLASK TOX METHOD, INTERIM METHOD 450.1, AND NEUTRON ACTIVATION ANALYSIS METHOD 9022

Sample Identification	Spike Level, mg/L	Average Halide Amount Found for Given Method, mg/L			Average Percent Recovery for Given Method		
		Schoeniger Flask TOX	Interim Method 450.1	Neutron Activation Analysis	Schoeniger Flask TOX	Interim Method 450.1	Neutron Activation Analysis
Reagent water	Unspiked	0.19	0.020	0.087	-- (a)	--	--
Reagent water	0.51	0.48	0.43	0.049	56	81	78
Groundwater #1	Unspiked	0.23	0.044	0.12	--	--	--
Groundwater #1	0.51	0.59	0.56	0.59	70	94	92
Groundwater #1	1.0	1.3	1.3	1.5	105	120	135
Groundwater #2	Unspiked	1.3	1.7	2.7	--	--	--
Groundwater #2	5.1	4.2	4.0	7.2	58	45	88
Groundwater #2	10.2	7.9	8.2	10.1	65	64	72

(a) Not applicable.

The results for the analyses of comparable samples using Interim Method 450.1 (Table 20) show recoveries ranging from an average of 45 percent to 120 percent and relative standard deviations of 17 percent or less for spiked reagent water and groundwater analyses.

The result of chloride and bromide analyses using the neutron activation analysis method (Tables 22 and 23, respectively) showed the best percent recovery values of the three methods, with average recoveries ranging from 72 to 140 percent for chloride analyses and from 75 to 103 percent for bromide analyses. The relative standard deviations ranged from 1.9 to 15 percent for chloride and from 2.1 to 28 percent for bromide.

The agreement for spiked samples was good for all three methods, as shown in Table 24 at levels above 0.2 mg/L halide. Unspiked halide levels for the Schoeniger flask TOX method were much higher for reagent water and groundwater #1 than either of the other methods due to the high average blank levels encountered with this method. Reagents and materials used in the preparation of those samples generally produce a blank level of approximately 20 µg of halide. The spike levels used were equivalent to only 50 µg of halide per 100 mL of sample, in the lowest level of spiked samples, or about two and one-half times the average reagent blank.

TASK 4: EVALUATION OF INSTRUMENTAL METHODS

The results of selected spiked charcoal samples analyzed using EPA Method 9022, Total Organic Halide by Neutron Activation Analysis, are presented in Table 25 for the chloride recoveries and in Table 26 for the bromide recoveries.

The chloride recoveries shown in Table 25 ranged from 91 percent for the low level spiked samples to 87 percent for the high-level spiked sample. The bromide recoveries (Table 26) ranged from 90 percent for the low-level spiked samples to 88 percent for the high-level spiked sample. The recoveries appeared to be consistently low by about 10 percent for both bromide and chloride as determined by the activation analysis procedure possibly due to losses in transport from Columbus, Ohio to the Battelle Pacific Northwest

TABLE 25. RESULTS OF CHLORIDE RECOVERY FROM SPIKED GRANULATED ACTIVATED CHARCOAL USING METHOD 9022, TOTAL ORGANIC HALIDE BY NEUTRON ACTIVATION ANALYSIS

Sample Identification	Spike Level, µg Chloride	(µg of Chloride Found in Given Sample)						Average Percent Recovery	Copper Flux Monitor Ratio[a]			
		Rep 1	Rep 2	Rep 3	Average	SD	RSD %		Rep 1	Rep 2	Rep 3	Average
Container blank	0	0.602	--[b]	--	0.603	--	--	NA[c]	1.28	--	--	1.28
Blank charcoal & container	0	1.92	2.04	--	1.98	0.08	4.3	NA	1.00	0.982	--	0.991
Spiked charcoal, Level 1	4.5	5.92	6.10	6.22	6.08	0.15	2.5	91	1.01	0.998	1.03	1.01
Spiked charcoal, Level 2	9.0	10.2	10.2	--	10.2	0.0	0.0	91	1.01	1.03	00	1.02
Spiked charcoal, Level 3	22.5	22.0	--[b]	--	22.0	--	--	89	1.03	--	--	1.03
Spiked charcoal, Level 4	72.0	64.8	--[b]	--	64.8	--	--	87	0.996	--	--	0.996
NBS Coal SRM 1632	880[d]	804	956	--	880	107	12.2	100	1.01	1.01	--	1.01

(a) Relative to one calibration standard.
(b) Only one replicate for the container blank and the two highest level spikes.
(c) Not applicable.
(d) Certified value. Sample was not spiked.

TABLE 26. RESULTS OF BROMIDE RECOVERY FROM SPIKED GRANULATED ACTIVATED CHARCOAL USING METHOD 9022, TOTAL ORGANIC HALIDE BY NEUTRON ACTIVATION ANALYSIS

Sample Identification	Spike Level, µg Bromide	(µg of Bromide Found In Given Sample) Rep 1	Rep 2	Rep 3	Average	SD	RSD, %	Average Percent Recovery
Container blank	0	0.04	--[a]	--	0.04	--	--	NA[b]
Blank charcoal & container	0	0.008	0.06	--	0.07	--	--	NA
Spiked charcoal, Level 1	0.5	0.492	0.514	0.554	0.520	0.031	6.0	90
Spiked charcoal, Level 2	1.0	0.983	0.950	--	0.966	0.023	2.4	90
Spiked charcoal, Level 3	2.5	2.33	--[a]	--	2.33	--	--	90
Spiked charcoal, Level 4	8.0	7.09	--[a]	--	7.09	--	--	88
NBS Coal SRM 1632	18[c]	17.2	19.2	--	18.2	1.41	7.8	100

(a) Only one replicate for container blank and the two highest level spike.
(b) Not applicable.
(c) Certified value. Sample was not spiked.

facility at Richland, Washington. Since two of the three spiked compounds were volatile, it is conceivable that these compounds were partially lost during shipment. The samples were shipped via UPS and were in transit for approximately 1 week.

Prior to the preparation of the spiked charcoal samples, the blank charcoal and the three component spiking solution were analyzed using the Dohrmann microcoulometric detector to determine the blank halide levels of the charcoal and to verify the concentration of the spiking solution. The results of these analyses showed that the blank charcoal contains 0.81 μg halide as chloride. A recovery of 99.6 percent for the spiking solution was obtained based upon the calculated halide content of the solution.

One step included in the analysis but not specified by the method was the use of a copper flux monitor for all samples to normalize all samples to the same neutron flux. The flux monitor results are presented in Table 25 with the chloride recoveries, where all flux monitor results have been normalized to a calibration standard. As shown in the table, all results for the copper flux monitors were within a few percent of each other with the exception of the flux monitor for the container blank.

The inclusion of the flux monitor option in the method should be considered since this practice offers some additional quality assurance on the measurement. However, considering the surrogate nature of the parameter being determined, the use of this option will increase the cost of the analysis and should only be used where very high precision and accuracy are desired or when it is known that the neutron source fluctuates considerably.

Another option which may be desirable for inclusion into the activation analysis method is the use of an equation which corrects for decay while the chloride or bromide is being counted. The half-lives of chlorine (37.3 min for $_{17}Cl^{38}$) and bromine (17.6 min for $_{35}Br^{80}$) are short enough that decay correction during counting may be significant.

The detection limit of the activation analysis determinative technique is limited by the blank halide levels in the granulated activated charcoal, which was found to be approximately 1.3 μg of chloride per 40 mg charcoal and 0.03 μg of bromide per 40 mg of charcoal. The blank halide level as

determined by the Dohrmann microcoulometric detector was found to be 0.8 μg as chloride.

TASK 5: EVALUATION OF WASTE OIL METHODOLOGY

The results of the analysis of the PCB-spiked oils using the sodium biphenyl/colorimetric chloride procedure are presented in Table 27. These results show a high positive bias in all cases, with recoveries ranging from a low of 145 percent to a high of 268 percent.

Since the unspiked oils were unavailable, it was not possible to correct the halide values from these sample extracts for anything other than the reagent blank halide level. This deficiency in blank correction probably accounts for a portion of the high recovery value for each sample.

In order to evaluate these high recoveries more thoroughly, an analytical curve study was performed by spiking a PCB-free transformer oil with Arochlor 1254, and the results of this study are presented in Table 28. These data show a high positive bias throughout, as measured by the average percent recovery. However, the bias ranges from 191 percent recovery for samples with no dilution to 115 percent recovery for samples with a 20-fold dilution. The magnitude of the positive bias appears to be reduced considerably with the value of the sample dilution.

The PCB-spiking solution concentration was verified by analysis using the Dohrmann microcoulometric detector, and the results are presented in Table 29. These data indicate that the concentration of the spiking solution was correct and is not the source of the high recoveries observed when using the sodium biphenyl/colorimetric chloride method.

One additional experiment was performed to evaluate the effect of dilution on the blank oil extract halide levels and the results of this experiment are shown in Table 30. These data show that for this particular transformer oil, the blank levels for a sample that has been diluted 10- or 20-fold are indistinguishable from the 0 ppm calibration standard. These results suggest that the blank level due to the oil can be removed through dilution, provided that the halide level is high enough for the sample to be diluted.

TABLE 27. RESULTS OF TOX ANALYSIS OF PCB-SPIKED OILS USING THE SODIUM BIPHENYL REAGENT - COLORIMETRIC CHLORIDE METHOD(a)

Identification	Arochlor Spiked	Spike Level, µg/g		Amount of Halide as Chloride Found In Given Replicate, µg/g						Average Percent Recovery
		As PCB	As Cl^-	Rep 1	Rep 2	Rep 3	Average	SD	RSD,%	
Transformer oil	none	0	0	26	27	27	27	0.57	2.2	--
Transformer oil	1254	100	54	140	130	120	130	10	7.8	190
Transformer oil	1254	500	270	340	340	400	360	36	9.8	120
Capacitor oil	1016(a)	507	81.1	283	308	292	294	12.7	4.3	347
Hydraulic oil	1016(a)	576	92.2	463	463	480	469	9.82	2.1	495
Hydraulic oil	1242(a)	574	241	665	640	635	647	16.1	2.5	268
Capacitor oil	1242(a)	51.4	21.6	37.9	36.5	37.9	37.4	0.81	2.2	173
Transformer oil	1254(a)	576	311	450	470	435	452	17.6	3.9	145
Hydraulic oil	1260(a)	576	346	630	680	585	632	47.5	7.5	183
Transformer oil	1260(a)	59.1	35.5	62.6	67.2	85.5	71.1	12.2	17	202

(a) These samples were acquired from the Quality Assurance Division of the US EPA at Cincinnati, Ohio.

TABLE 28. RESULTS OF ANALYTICAL CURVE STUDY ON TRANSFORMER OIL SPIKED WITH AROCHLOR 1254 USING THE SODIUM BIPHENYL REAGENT - COLORIMETRIC CHLORIDE METHOD

Sample Identification	Spike Level, µg/g of oil		Amount of Halide Found in Given Replicate, µg/g of oil							
	As PCB	As Chloride[a]	Rep. 1	Rep. 2	Rep. 3	Average	SD	RSD, %	Percent Recovery	Sample Dilution
Method Blank[b]	0	0	14	13	15	14	1.0	7.1	--	0
Unspiked oil	0	0	26	27	27	27	0.57	2.2	--	0
Spiked oil, level 1	100	54	114	101	94	103	10.1	9.8	191	0
Spiked oil, level 2[c]	250	135	188	186	--	187	1.4	0.76	138	2-Fold
Spiked oil, level 3	500	270	320	315	380	338	36	11	125	5-Fold
Spiked oil, level 4[c]	1000	540	660	672	--	666	8.5	1.3	123	10-Fold
Spiked oil, level 5[c,d]	2330	1260	1440	1460	--	1450	14	1.0	115	20-Fold

(a) A 54% by weight chloride content is assumed for Arochlor 1254.
(b) A sample weight of 2.5 g is assumed for the method blank in order to put the halide amounts in perspective with the oil values.
(c) Only two replicates processed for these data points.
(d) Sample weight was 10.77 g of oil instead of 12.5 g used in other samples.

TABLE 29. VERIFICATION OF HALIDE CONCENTRATION OF CHARCOAL AND HALIDE SPIKING SOLUTION USING THE DOHRMANN MICROCOULOMETRIC DETECTOR

Sample Identification	Amount Spiked, µg Halide	Amount Found in Given Replicate				Standard Deviation	RSD, %	Percent Recovery[a]
		Replicate 1	Replicate 2	Replicate 3	Average			
Method Blank[b]	0	0.05	--[c]	--	0.05	--	--	--
Blank charcoal	0	0.70	0.96	0.78	0.81	0.13	16	--
Spiked charcoal[d]	100	97.1	101.1	102.9	100.4	2.97	3.0	99.6[e]
PCB-spiked charcoal[f]	33.8	32.1	33.4	34.4	33.3	1.13	3.4	96.1

(a) Spiked charcoal only.
(b) Value obtained for analysis of a sample boat blank without charcoal.
(c) Dash indicates not analyzed or not applicable.
(d) Spiked with 5.0 µL of the 20 µg Halide/mL solution.
(e) Corrected for blank charcoal concentration.
(f) Spiked with 5.0 µL of the 12.5 mg/mL solution of Arochlor 1254 in toluene.

TABLE 30. EVALUATION OF THE EFFECT OF DILUTION ON BLANK HALIDE LEVELS USING AN UNSPIKED TRANSFORMER OIL EXTRACT

Dilution	Absorbance Reading for Given Replicate[a]			
	Replicate 1	Replicate 2	Replicate 3	Average
Undiluted extract	0.124	0.128	0.130	0.127
5-Fold dilution	0.045	0.049	--[b]	0.047
10-Fold dilution	0.034	0.036	--[b]	0.035
20-Fold dilution	0.031	0.024	--[b]	0.027
0.0 ppm Calibration Standard	0.030	0.031	0.034	0.034

(a) All absorbance values obtained using deionized water to set 0.0 absorbance.
(b) Only two replicates analyzed for these data points.

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APPENDIX A

TEST METHOD
TOTAL ORGANIC HALIDES (TOX) BY SCHOENIGER
FLASK OXIDATION AND COLORIMETRIC
HALIDE ANALYSIS

1. SCOPE AND APPLICATION

1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption in drinking, ground, and surface waters. The term organic halides as used in this method is defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method.

1.2 The method uses a carbon adsorption procedure identical to that of U.S. EPA Method 450.1, sample preparation using Schoeniger flask oxidation, and colorimetric chloride quantification using ASTM Method D-512. When this method is used to analyze unfamiliar samples, it should be supported by at least one additional qualitative technique.

1.3 The method detection limit (MDL, defined in Section 15.1)(1) is listed in Table 1. The MDL for a specific water sample may differ depending upon the nature of the interferences in the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of carbon adsorption procedures for sample concentration, oxygen flask combustion for sample preparation, and in the use of colorimetric methods of analysis.

2. SUMMARY OF METHOD

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids is passed through a column containing 40 mg of granulated activated carbon (GAC). The column is washed to remove any trapped inorganic halides, and is then combusted in a Schoeniger flask

to convert the adsorbed organohalides to inorganic halide. The halides are then determined using a colorimetric method.

3. INTERFERENCES

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400 C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg apparent halide should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic halide concentration does not exceed the organic halide concentration by more than 20000 times.

4. SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness

file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (2-4) for the information of the analyst.

5. APPARATUS AND MATERIALS (All specifications are suggested). Catalog numbers are included for illustration only.

5.1 SAMPLING EQUIPMENT, FOR DISCRETE OR COMPOSITE SAMPLING

5.1.1 Grab-sample bottle - Amber glass, 250 mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400 C before use to minimize contamination.

5.2 ADSORPTION SYSTEM

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized with prepurified nitrogen, with sample and nitrate-wash reservoirs, and all required accessories. A general schematic of the adsorption system is shown in Figure 1.

5.2.2 Adsorption columns - pyrex, 5-cm long x 6-mm OD x 2-mm ID.

5.2.3 Adsorption column housing assembly (available from Dohrmann) - for holding and coupling the pyrex adsorption columns.

5.2.4 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon analysis of 40 mg of GAC, the apparent halide background should be 1000-ng Cl^- equivalent or less.

5.2.5 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. Do not touch this material with your fingers.

5.3 SCHOENIGER FLASK COMBUSTION APPARATUS

5.3.1 Thomas-Ogg 1000 mL combustion flask, or equivalent (available from Arthur H. Thomas, 6514-F20).

5.3.2 Ogg type platinum sample carrier (available from Arthur H. Thomas, 6514-F45).

5.3.3 Sample wrappers, black (available from Arthur H. Thomas, 6514-F70). Cut into strips that are approximately 0.5 cm x 5 cm for use as a fuse for igniting samples.

5.3.4 Filter paper, Whatman 541 or equivalent. Cut to 3 x 3 cm squares for wrapping granulated activated charcoal from adsorption module.

5.3.5 Oxygen flask igniter (optional) - a focused 150 watt infrared lamp (available from Arthur H. Thomas, 6516-510).

5.4 SPECTROPHOTOMETRIC APPARATUS

5.4.1 Spectrophotometer - Bausch and Lamb Spectronic 20 or equivalent.

5.4.2 Sample cuvettes - for use with above spectrophotometer (10 mm ID or larger).

5.4.3 Class A volumetric flasks for use in preparing calibration curves and sample dilutions (various sizes).

5.4.4 Class A volumetric pipets - various sizes from 0.5 to 25 mL, for use in preparing calibration curves, sample aliquoting, and sample dilutions.

5.4.5 Filtration apparatus (optional) - Millipore Millex-GS (0.22 µm) or equivalent, with 10 mL disposable syringes, for use in filtering samples to remove particulate matter after combustion.

6. REAGENTS

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.1.1 Reagent water can be generated by passing deionized water from a water purification system (Millipore Super-Q or equivalent) through a carbon filter bed containing about 1 pound of activated carbon Filtrasorb-300 or equivalent (Calgon Corp) .

6.2 Sodium thiosulfate - 0.1 M, ACS reagent grade (12.6 g/L).

6.3 Nitric acid - concentrated.

6.4 Nitrate-Wash Solution (5g NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-liter volumetric flask and diluting to volume with reagent water.

6.5 Nitrogen - Prepurified for use in pressurizing the adsorption module reservoirs.

6.6 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.7 Trichlorophenol standard, adsorption-efficiency and laboratory control standard (1000 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 100 µL of stock solution into 1 liter of reagent water.

6.8 Blank standard - The reagent water used to prepare the adsorption efficiency standard (see Section 6.7).

6.9 Potassium hydroxide - 0.1 M, ACS reagent grade (5.61 g/L) in reagent water.

6.10 Ferric Alum solution - Dissolve 5.0 g of ferrous ammonium - sulfate ($Fe(NH_4)_2(SO_4)_2$ $6H_2O$) in 20 mL of water. Add 38 mL of concentrated nitric acid (HNO_3, sp gr 1.42) and boil to oxidize the ferrous ion and remove the oxides of nitrogen. Dilute to 100 mL with halide-free water.

6.11 Mercuric Thiocyanate, Methanol Solution (3 g/liter) - Dissolve 0.30 g of mercuric thiocyanate ($Hg(CNS)_2$) in 100 mL of methanol. Store in amber bottles. Allow to stand for at least 24 hr before using. A slight precipitate may form and settle out after the 24 hr. Care must be taken so that this precipitate is not resuspended when using the reagent. Only the clear, supernatant liquid must be used. Do not use if more than 4 weeks old.

6.12 Sodium Chloride, Standard Solution (100 mg Cl^-/liter) - Dry several grams of sodium chloride (NaCl) for 1 hr at 600 C. Prepare a stock solution by dissolving exactly 1.649 g of the dry salt in water and dilute to 1 liter. Prepare the standard solution as needed by diluting 10.0 mL of the stock solution to 100.0 mL with halide free water.

7. CALIBRATION

7.1 Prepare calibration standards at a minimum of five concentration levels by carefully adding 5.0, 10.0, 15.0, 20.0, and 25.0 mL of the 100 mg/L standard chloride solution from 6.12 to each of five 100 mL class A volumetric flasks and diluting to volume with halide free reagent water. A zero level standard of the halide free dilution water is also prepared by adding 100 mL of the water to a volumetric flask.

7.2 Analyze each calibration standard according to Section 13, and tabulate the absorbance or percent transmittance of each standard versus the concentration in the standard. These data are used to prepare a calibration curve for chloride ion.

7.3 The working calibration curve must be prepared on each working day along with the samples to be measured.

7.4 Check the adsorption efficiency of each newly prepared batch of carbon by analyzing 100 mL of the adsorption efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.5 Method Blanks - Establish the repeatability and reagent background of the method each day by first analyzing at least two method blanks, prepared in accordance with Section 8.1.2. Monitor this background by spacing method blanks between each group of ten determinations.

8. QUALITY ASSURANCE

8.1 MONITORING FOR INTERFERENCES

8.1.1 Field Blanks - A field blank is a sealed bottle of reagent water that accompanies a set of sample bottles from the laboratory to collection sites and back. Analyze a field blank along with each sample set.

8.1.2 Method Blanks - A method blank is a 100-mL aliquot of reagent water prepared and analyzed as if it were a sample, and contains all reagents and materials that

are used for an authentic sample. If a method blank contains a reportable level of analyte, the samples must be corrected for the blank amount.

8.2 ASSESSING ACCURACY

8.2.1 Accuracy with this method is determined by the analysis of laboratory control standards. Laboratory control standards may be prepared solely from concentrates provided and certified by external sources, or in combination with concentrations prepared in the laboratory.

8.2.2 After every 10 samples, and preferably in the middle of each day, analyze a laboratory control standard. Calibration standards may not be used for accuracy assessments and laboratory control standards may not be used for calibration of the analytical system.

8.2.2.1 Analyze a 100 mL aliquot of the laboratory control standard (Section 6.7) as described in Sections 10, 11, 12, and 13. Calculate the percent recovery (P_i) as follows:

$$P_i = \frac{100\ S_i}{T_i}$$

where: S_i = the analytical result from the laboratory control standard, in mg/L.

T_i = the known concentration of the spike, in mg/L.

8.3 ASSESSING PRECISION

8.3.1 Precision assessments for this method are based upon the analysis of duplicate samples. Duplicate samples should be analyzed in every set of 10 samples.

8.3.2 For each duplicate pair, calculate the relative range (RR_i):

$$RR_i = \frac{100\ R_i}{X_i}$$

where: R_i = the absolute difference between the duplicate measurements X_1 and X_2, in mg/L.

X_i = the average concentration found $(X_1 + X_2)/2$, in mg/L.

8.3.3 Individual relative range measurements are pooled to determine the average relative range or to develop an expression of relative range as a function of concentration. Report precision assessments with all analytical results.

9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 All samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (1 mL of 0.1 M per liter of sample) to the empty sample bottle just prior to shipping to the sampling site. U.S. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.(6) Field test kits are available for this purpose.

9.2 Grab samples must be collected in glass containers having a total volume of at least 100 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be analyzed within 14 days of collection.

10. SAMPLE PREPARATION

10.1 Special care should be taken in the handling of the sample to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

10.2 It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4 C without headspace.

10.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the adsorption module sample reservoir.

11. ADSORPTION PROCEDURE

11.1 Connect the two adsorption columns in series using the adsorption column housing assembly, with each column containing 40 mg of 100/200-mesh activated carbon.

11.2 Fill the sample reservoir (Figure 1), and pass a metered amount of sample through the activated carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 500 and 2500 µg/L; 50 mL for 2501 to 5000 µg/L, and 25 mL for 5001 to 10,000 µg/L.

11.3 Wash the columns in series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

12. CHARCOAL COMBUSTION PROCEDURE

12.1 Transfer the 40 mg of GAC from the primary adsorption column onto the 3 x 3 cm square of filter paper and wrap securely by folding the paper over the sample so that the entire sample is wrapped with as many layers of paper as the paper size permits. The second (backup) adsorption column charcoal should be retained until analysis of the primary column is completed for possible breakthrough evaluation.

CAUTION: DO NOT TOUCH THE WRAPPING PAPER WITH BARE FINGERS. DISTILLED WATER RINSED RUBBER GLOVES SHOULD BE USED.

12.2 Clip the paper with a small paper clip and place in an open 1-oz vial in a dessicator for at least 4 hours to dry prior to combustion.

12.3 When dry remove the clip holding the sample wrapping paper, and carefully place the sample in the platinum sample carrier and attach the 0.5 cm x 5 cm black filter paper starter to the sample in the platinum holder. Suspend the platinum holder on the combustion flask stopper.

12.4 Add 10.0 mL of the 0.1 M KOH solution to the 1000 mL combustion flask and place the sample carrier assembly (Section 5.3.2) on the flask.

12.5 Using a small 30 cm glass tube or disposable 1 mL glass graduated serological pipet attached to the oxygen supply line, flush the combustion flask containing the KOH and sample with a rapid flow of oxygen (approximately 1 liter/minute) for 5 minutes by inserting the glasstube through the top of the flask between the flask and the sample carrier assembly, with the gas delivery tube positioned near the bottom of the flask in order to displace air.

12.6 Remove the oxygen supply tube and quickly seal the flask with the sample carrier assembly and the flask clamp.

12.7 Ignite the black paper starter using the infrared lamp. Once combustion is complete, the flask must be vigorously shaken periodically and allowed to stand for at least 60 minutes in order for the vapors to be completely absorbed by the KOH solution. Alternatively, if the infrared oxygen flask ignitor (Section 5.3.5) is not available, the sample starter paper can be ignited from an external flame (CAUTION) by the following procedure: remove the oxygen supply tube from the flask. Ignite the sample starter paper (Section 5.3.3) from a carefully controlled flame, and insert the sample carrier assembly into the combustion flask. Secure with the flask clamp.

12.8 After absorption, transfer the 0.1 M KOH solution to a clean vial equipped with a Teflon-lined screw cap for storage prior to analysis.

13. COLORIMETRIC HALIDE DETERMINATION

13.1 Transfer 5.0 mL of the 0.1 M KOH adsorption solution or calibration solution from the combustion procedure to a clean, dry 50-mL test tube and add successively 1.0 mL of ferric alum solution and 0.5 mL of mercuric thiocyanate solution. If the sample solution is cloudy due to particulates from combustion, filter using the fitration apparatus described in Section 5.4.5 prior to aliquoting and adding the color developing reagents. Mix thoroughly and allow to stand for 10 minutes.

13.2 Adjust the zero setting of the spectrophotometer prior to making any calibration readings by using 5.0 mL of halide free reagent water prepared in accordance with 13.1.

13.3 Measure the intensity of the color formed for the sample solution at a wavelength of 463 nm, and determine the concentration from the calibration line prepared in accordance with steps 7.1 through 7.3. For samples which contain high levels of chloride ion, it is necessary to make an appropriate dilution of the sample such that the absorbance or percent transmittance reading obtained is within the absorbance range of the calibration standards. Method blanks should be analyzed at equivalent dilutions for appropriate background correction. For high level chloride samples, the backup adsorption column charcoal should be analyzed as described in Sections 12 and 13 to check for breakthrough of halides from one column to another. All second-column measurements for a properly operating system should not exceed 10 percent of the two-column total measurement. If the 10 percent figure is exceeded, one of three events can

have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained in which case taking a smaller sample may be necessary; or channeling or some other failure occurred in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun.

14. CALCULATIONS

TOX as Cl^- is calculated using the following formula:

$$\frac{[(C_1-C_3)+(C_2-C_3)]\ 10\ D}{V} = \text{mg/L Total Organic Halide}$$

where:
C_1 = µg/mL Cl^- in the digest from the first column in series
C_2 = µg/mL Cl^- in the digest from the second column in series
C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column), in µg/mL Cl^-
V = the sample volume in mL
D = dilution factor for diluted samples
10 = total volume of column digest in mL.

15. METHOD PERFORMANCE

15.1 Method Detection Limit - the method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero (1). The MDL concentration for this method has been found to be 0.15 mg/L as chloride in reagent water when the average reagent background is no more than 0.20 mg/L as chloride.

15.2 In a single laboratory (Battelle Columbus Laboratories), using spiked groundwater, the average recoveries presented in Table 1 were obtained. Each sample was analyzed in triplicate, and the standard deviation of the percent recovery is also included in Table 1.

TABLE 1. SINGLE OPERATOR ACCURACY AND PRECISION

Sample	Average Percent Recovery	Standard Deviation, Percent	Spike Level, mg/L	Number of Analyses
A	70	18	0.15	3
A	105	9.5	1.0	3
B	58	5.3	5.0	3
B	65	7.2	10.0	3

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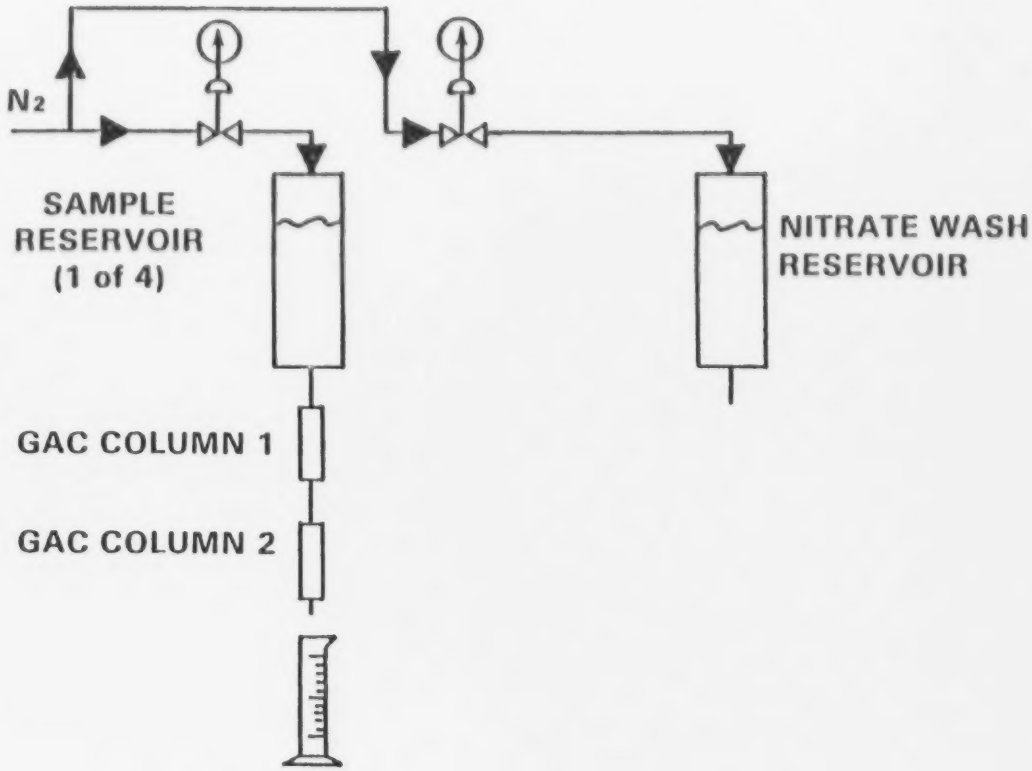

FIGURE 1. ADSORPTION SCHEMATIC.

APPENDIX B

METHOD 9022

TOTAL ORGANIC HALIDES (TOX) BY NEUTRON ACTIVATION ANALYSIS

1.0 Scope and Application

1.1 Method 9022 determines Total Organic Halides (TOX) in drinking, ground, and river waters, and in wastewater treatment plant effluents. The method uses a carbon adsorption procedure identical to that of Method 9020 (TOX analysis using a microcoulometric-titration detector), irradiation by neutron bombardment, then detection using a gamma-ray detector. All samples should be run in duplicate and the reliable limits of detection are 5 ppb for chlorine and 1 ppb for iodine and bromine.

1.2 Method 9022 detects all organic halides containing chlorine, bromine, iodine, and fluorine that are adsorbed by granular activated carbon under the conditions of the method. Each halogen can be quantitated independently.

1.3 Method 9022 is restricted to use by, or under the supervision of, analysts experienced in the operation of neutron activation analysis and familiar with spectral interferences.

1.4 This method may be used in place of Method 9020 and has the advantage of determining the individual concentrations of the halogens chlorine, bromine, and iodine in addition to TOX.

2.0 Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of granulated activated carbon (GAC). The column is washed to remove any trapped inorganic halides. The GAC sample is exposed to thermal neutron bombardment creating a radioactive isotope. Gamma-ray emission, which is unique to each halogen, is counted. The area of the resulting peaks is directly proportional to the concentration of the halogens.

3.0 Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution.

This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400° C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 It is possible that other radioisotopes, stray radiation, counting geometries, and counting-equipment materials can affect gamma counting. It is essential that the data interpretation be performed by an analyst experienced at detecting these interferences.

4.0 Apparatus and Materials

4.1 Adsorption system

4.1.1 Dohrmann adsorption module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.2.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000 ng Cl^- equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville), or equivalent: Form this material into plugs using a 2-mm-I.D. stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

4.1.5 Column holders (available from Dohrmann).

4.1.6 Volumetric flasks: 100-ml, 50-ml. A general schematic of the adsorption system is shown in Figure 1.

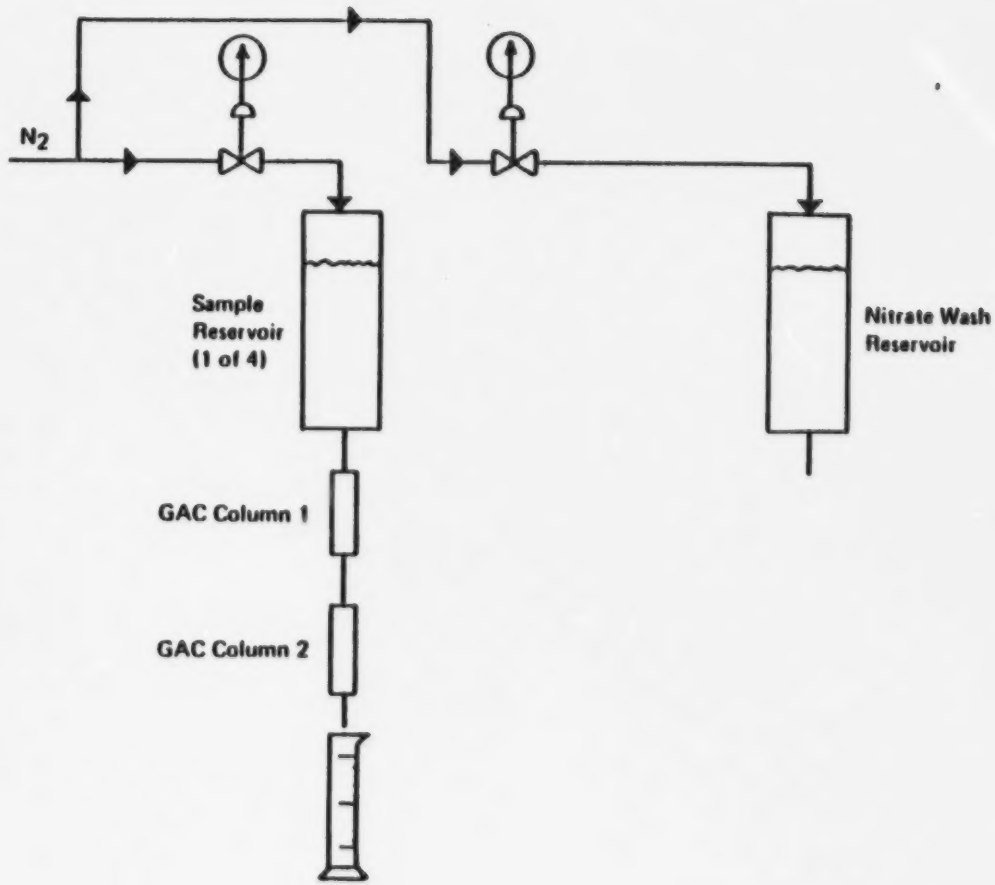

Figure 1. Schematic of Adsorption System.

4.2 Containers suitable for containment of samples and standards during irradiation (e.g., 1/5-dram polyethylene snap-cap vial).

4.3 Sample introduction system and a reactor generating a thermal neutron flux capable of achieving enough halogen activity for counting purposes (e.g., a reactor having a neutron flux of 5×10^{12} neutrons/cm^2/sec and a pneumatic-tube sample introduction system).

4.4 A gamma-ray detector and data handling system capable of resolving the halogen peaks from potential interferences and background.

5.0 Reagents

5.1 Prepurified nitrogen.

5.2 Deionized water.

5.3 5000 ppm NO_5 solution (KNO_3 dissolved in DI water).

5.4 50% v/v mixture acetone and nanograde hexane.

5.5 0.1 M sodium sulfate (ACS reagent grade - 12.6 g/l).

5.6 Nitric acid: concentrated, reagent grade.

5.7 25-µg Cl, 2.5-µg Br, and 2.5-µg I standards.

5.8 Radioactive standards to be used for calibrating gamma-ray detection systems.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples should be collected in bottles with teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass, 250-ml, fitted with teflon-lined caps. Foil may be substituted for teflon if the sample is not corrosive. Samples must be protected against loss of volatiles by eliminating headspace in the container. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400° C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in 3.1.1.

7.0 Procedure

7.1 Sample preparation

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

7.1.2 Reduce residual chlorine by adding sulfite (1 ml of 0.1 M per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4° C without headspace.

7.1.3 Adjust the pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

7.2 Calibration

7.2.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 ml of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.2.3 Prior to each day's operation, the instrument is calibrated using radioactive standards (e.g., cobalt-60 and radium-226 sources). The instrument is calibrated such that both gamma rays from the standards fall within plus or minus one channel of their true energies. A 100-sec blank is then counted to verify that no stray radioactive sources are within sensing distance of the detector. As data are obtained throughout the day peak locations in the standards are monitored to ensure there is no electronic drift of the instrument. If drift is noted, the system is recalibrated.

7.3 Adsorption procedure

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately

3 ml/min. NOTE: 100 ml of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/l; 50 ml for 501 to 1000 µg/l, and 25 ml for 1001 to 2000 µg/l.

7.3.3 Wash the columns-in-series with 2 ml of the 5000-mg/l nitrate solution at a rate of approximately 2 ml/min to displace inorganic chloride ions.

7.4 Activation

7.4.1 After the quartz collection tube with the GAC is removed from the extraction unit, the GAC and cerafelt pads are extruded using the packing rod into a prewashed plastic container (e.g., 1/5-dram polyethylene snap-cap vial). The vial is prewashed to remove inorganic and organic chorine by soaking in distilled water followed by storage in a glass jar containing 50% v/v acetone and hexane. Just prior to extrusion the vial is removed by forceps and air-dried to remove residual water, acetone, and hexane. The vial is snapped shut, the hinge removed with a scalpel blade, the cap heat-sealed to the vial with an electric soldering gun reserved for that purpose, and a single-digit number placed on the vial with a Marks-A-Lot (or equivalent) marker pen.

7.4.2 Samples plus a similar vial containing 25 µg Cl, 2.5 µg Br and 2.5 µg I standards are then introduced into the reactor, generally by placing them together in a 5-dram polyethylene vial and inserting them into a pneumatic-tube transfer "rabbit" for neutron irradiation. Irradiation would be for a 15-min period at a thermal neutron flux of 5×10^{12} neutrons/cm^2/sec. After returning from the reactor the rabbit is allowed to "cool" for 20 min to allow short-lived radioisotopes (primarily Al) present in the GAC to decay away.

7.5 Detection

7.5.1 Analysis is performed using a gamma-ray detector such as a 55-cm^3 Princeton Gamma Tech lithium drifted germanium (Ge Li) detector with an Ortec Model 451 amplifier and a 4096-channel Nuclear Data 2200 memory unit for data storage. The analyses can be performed either manually, with the operator changing samples and transferring the data to magnetic tape, or automatically, with both functions performed by an automatic sample changer.

7.5.2 Analysis begins by counting the standard and samples for a suitable time period (e.g., 200 sec "live" time for the standards and samples). The operator records the time intervals between samples and the "dead" time of each sample in a logbook for later use in calculating halogen concentrations in each sample.

7.6 Calculations

7.6.1 Chlorine, bromine, and iodine can be analyzed within a 200-sec counting period taking place 20 to 40 min after irradiation.

7.6.2 Chlorine is analyzed using the 1642-KeV gamma ray produced by 37.1-min ^{38}Cl. Bromine is analyzed using the 616-KeV gamma ray from 17.7-min ^{80}Br, while iodine is analyzed using the 442-KeV gamma ray produced by 25-min ^{128}I.

7.6.3 The calculation used for quantitation is:

$$\text{ppm halogen} = \frac{\text{cts unk.}}{\text{cts std.}} \times \frac{\text{counting time std.}}{\text{counting time unk.}} \times \frac{\mu\text{g in std.}}{\text{sample vol.}} \times e^{\lambda t}$$

where

cts unk. = the integrated area of the appropriate gamma-ray peak in the unknown with background subtracted and the total multiplied by 1 + [(% dead time unknown - % dead time std.)/200]. The latter correction is usually less than 4% and corrects for pile-up errors.

cts std. = the integrated area of the appropriate gamma-ray peak in the standard with background subtracted.

counting time std. = the "live" counting time in seconds of the standard.

counting time unk. = the "live" counting time in seconds of the unknown.

µg in std. = the number of micrograms of the stable element in question in the standard (25 for Cl, 2.5 for Br and I).

sample vol. = the volume of sample passed through the GAC column, in milliliters.

$e^{\lambda t}$ = The decay correction to bring all statistics back to t = 0. $\lambda = 0.693/t_{1/2}$ where $t_{1/2}$ = the half-life, in minutes.

t = the time interval in minutes from the end of the count of the standard until the end of the count of the sample.

7.6.4 No further calculations are necessary as long as the final sample is counted within 40 min after the end of irradiation. If samples are counted after 40 min, the addition to the 616-KeV peak of ^{80}Br from the 619-KeV peak from ^{82}Br becomes large enough that a correction factor must be applied. In practice all counting should be completed in less than 40 min after irradiation.

8 / MISCELLANEOUS ANALYTICAL METHODS

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by analyzing appropriate quality-control check samples.

8.3 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Run check standard after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparations process.

8.7 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

8.8 Quality control for the analysis phase is very straightforward since the instrument is a noncontact analyzer. That is, only the radiation emitted from the sample - not the sample itself - should touch the analyzer. Since contamination of the system is not usually a problem (unless a sample spills on it), the most serious quality-control issues deal with uniform neutron flux, counting geometry, and spectral interpretation. The amount of radioactivity induced in a sample is directly proportional to the neutron flux it is exposed to. Since this flux can vary depending on how the sample is positioned in relation to the reactor core during irradiation, it is essential that a known standard be irradiated with every sample batch to act as a flux monitor. Care must also be taken to ensure that the standard and all samples associated with the standard are counted at the same distance from the detector.

United States
Environmental Protection
Agency

EPA

Research and Development

Total Organic Halide
Method 450.1 - Interim

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APPENDIX C

TOTAL ORGANIC HALIDE

Method 450.1

Interim

U. S. Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Physical and Chemical Methods Branch
Cincinnati, Ohio 45268

November 1980

TOTAL ORGANIC HALIDE

Method 450.1

1. Scope and Application

1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/L. Organic halides as used in this method are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine containing species are not determined by this method.

1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed

to remove any trapped inorganic halides, and is then pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply

should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

4. Safety

The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400°C before use, to minimize contamination.

5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000-ng Cl^- equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

6. Reagents

6.1 Sodium sulfite - 0.1 M, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng Cl^-) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 Trichlorophenol standard, instrument-calibration - First, nitrate wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 Reagent water - Reagent water is defined as a water in which an

interferent is not observed at the method detection limit of each parameter of interest.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 mL of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2 Nitrate-wash blanks (Method Blanks) - Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations.

7.2.1 The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to

minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at $4^{o}C$ without headspace.

8.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L; 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L.

9.3 Wash the columns-in-series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

10. Pyrolysis Procedure

10.1 The contents of each column is pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at 800°C for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the 200°C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

13.3 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

14. Calculations

OX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in L

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

Model Compound	Dose µg/L	Dose as µg/L Cl	Average % Recovery	Standard Deviation	No. of Replicates
$CHCl_3$	98	88	89	14	10
$CHBrCl_2$	160	106	98	9	11
$CHBr_2Cl$	155	79	86	11	13
$CHBr_3$	160	67	111	8	11
Pentachlorophenol	120	80	93	9	7

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

Sample	Avg. halide ug Cl/L	Standard Deviation	No. of Replicates
A	71	4.3	8
B	94	7.0	6
C	191	6.1	4

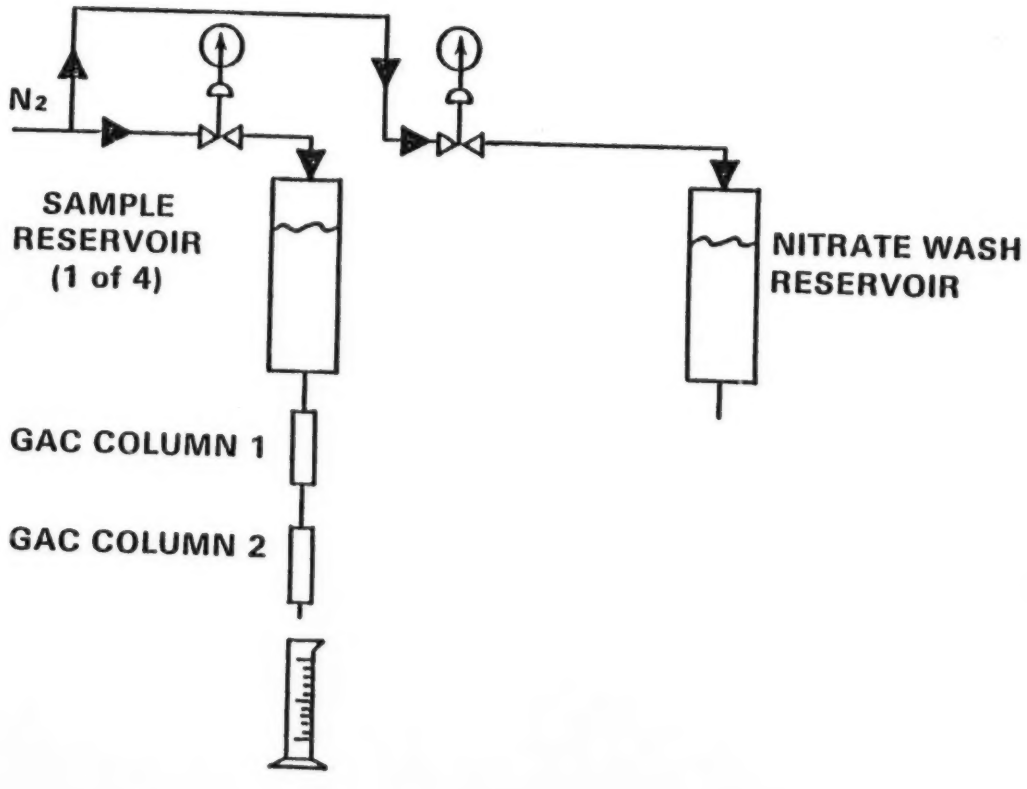

Figure 1. Adsorption Schematic

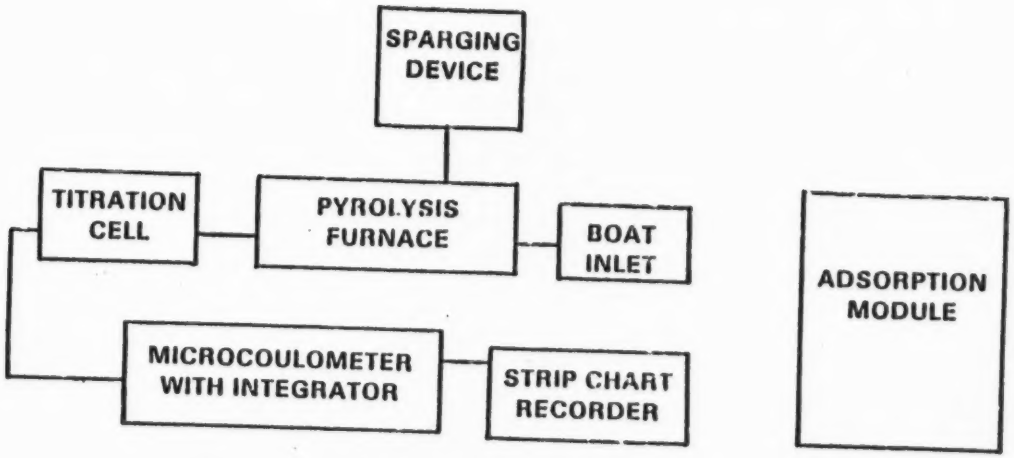

Figure 2. CAOX Analysis System Schematic

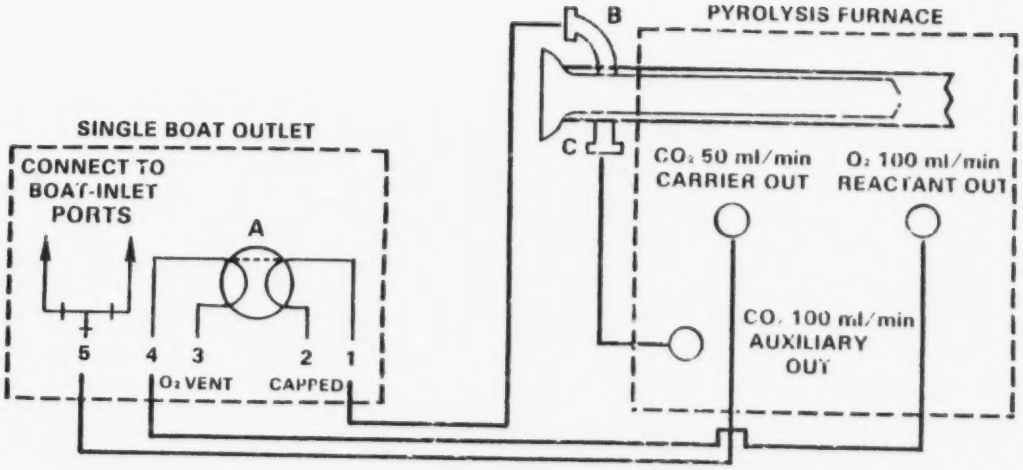

Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.